PB81-172306

Analytical Methods Evaluation for Applicability in Leachate Analysis

Washington Univ.
Seattle

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Mar 81

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA 600/2-81-046	2.	3. RE PB81-172306
4. TITLE AND SUBTITLE Analytical Methods Evaluation For Applicability in Leachate Analysis		5. REPORT DATE March 1981 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) DeWalle and Sanning et al		8. PERFORMING ORGANIZATION REPORT NO. none
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Environmental Health University of Washington Seattle, Washington 98195		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. Grants R804883 and R805753
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory - Cin., OH Office of Research and Development U. S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Final 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer-Donald E. Sanning 513/684-7871

16. ABSTRACT

In this study a round robin analysis of 10 leachate samples was conducted by 32 laboratories in the United States and Canada. Samples were analyzed for up to 28 parameters, including physical parameters (ph, oxidation reduction potential, conductivity, turbidity, and residue), organics (chemical oxygen demand, total organic carbon, organic nitrogen, and free volatile fatty acids), anions (sulfate, phosphate, chloride, nitrate, and bicarbonate), and cations (alkali metals, alkaline earth metals, transition metals, and heavy metals).

It was noted that the overall coefficients of variation ranged from 32% for the chemical oxygen demand to 210% for the cadmium determination. Significant differences were noted between results from colorimetric methods and titrimetric and physical methods. The average recovery for spiked parameters in one leachate sample was 81% but varied widely for individual parameters. Results obtained using automated methods commonly deviated from those of other methods.

Recommendations were made for selection of the most applicable method for analysis of each parameter. The usage of the standard addition technique is required in each laboratory to determine the matrix depression or enhancement for each type of leachate sample.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Methodology Selection Assessment Tests Interpretation Evaluation	Methods Leachate Leach Test	14B

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified 20. SECURITY CLASS *(This page)* Unclassified	21. NO. OF PAGES 340 22. PRICE

EPA Form 2220-1 (9-73)

PRODUCT OF:
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

PB81 172306

EPA-600/ 2-81-046
March 1981

ANALYTICAL METHODS EVALUATION FOR APPLICABILITY IN LEACHATE ANALYSIS

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

In this study a round robin analysis of 10 leachate samples was conducted by 32 laboratories in the United States and Canada. Estimates were established for the between laboratory and within laboratory coefficients of variation or standard deviations.

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ABSTRACT

In this study a round robin analysis of 10 leachate samples was conducted by 32 laboratories in the United States and Canada. Samples were analyzed for up to 28 parameters, including physical parameters (pH, oxidation reduction potential, conductivity, turbidity, and residue), organics (chemical oxygen demand, total organic carbon, organic nitrogen, and free volatile fatty acids), anions (sulfate, phosphate, chloride, nitrate, and bicarbonate), and cations (alkali metals, alkaline earth metals, transition metals, and heavy metals).

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Recommendations were made for selection of the most applicable method for analysis of each parameter. The usage of the standard addition technique is required in each laboratory to determine the matrix depression or enhancement for each type of leachate sample.

This report was submitted in fulfillment of Grant R805753 by the University of Washington, Department of Environmental Health, and of Grant R804883 by Stanford University, Department of Civil Engineering, under sponsorship of the U.S. Environmental Protection Agency.

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ACKNOWLEDGMENTS

The support of the Solid and Hazardous Waste Research Division of the Municipal Environmental Research Laboratory is acknowledged with sincere thanks. Major contributions were made by Donald Sanning, Richard Carnes, and Dirk Brunner of the Solid and Hazardous Waste Research Division and by John Winter of the Quality Assurance Branch. Participation of the 32 laboratories is sincerely acknowledged, as without their cooperation this study would not have been possible.

The present study is an extension of the study "Compilation of Methodology used for Measuring Pollution Parameters of Sanitary Landfill Leachate," Contract CI 68-03-2052, conducted by Edward Chian, currently at Georgia Institute of Technology, and Foppe DeWalle at the University of Illinois. The latter author conducted the first half of the present study at Stanford University, under the direction of Perry McCarty and assisted by Michael Bissell and Kim Hayes, and the second half at the University of Washington. The statistical calculations and the corresponding report text were prepared by Theodore Zeisig, assisted by Donald Norman. The chemical analyses were conducted by Michael Bissell and Kim Hayes at Stanford University, and by John Sung at the University of Washington. Jack Hatlen, the coordinator of the environmental health section of the department, greatly facilitated the present study.

SECTION 1

INTRODUCTION

Monitoring solid waste disposal sites is important in assessing environmental impact on surface water and groundwater. Further precise and accurate physical and chemical methods of analysis should be available to measure the degree of pollution. Recently completed and ongoing studies by the Solid and Hazardous Waste Research Division have identified certain problem areas in analytical methods as presently applied to leachate analyses. The official EPA analytical methods (EPA, 1974) and Standard Methods (APHA, 1971) were primarily developed for analysis of water and wastewater, and their direct application to leachate analysis can lead to erroneous results. It was therefore the purpose of the present study to conduct an in-depth evaluation of both the accuracy (i.e., agreement between measured and actual amounts) of different chemical methods, and the precision (i.e., reproducibility) of these methods. The precision determination involved participation of 32 laboratories, each of which determined a maximum of 28 parameters in 10 representative leachate samples. The data generated in the collaborating laboratories were then used to determine the precision of each method.

SECTION 2

CONCLUSIONS

In the present study the overall coefficient of variation, defined as the standard deviation as percentage of the average, ranged from 32% for the chemical oxygen demand determination to 210% for the cadmium determination. The between laboratory component of the variation was larger than the within laboratory component. The largest portion of the variation, however, was due to a sample laboratory interaction, i.e. the relative results of the laboratories change for different leachate samples.

Further, the results of the leachate analysis more closely resembled a lognormal distribution than a normal distribution, and the standard deviation of the data in the lognormal scale is equivalent to the coefficient of variation of the data in the original scale of measurement as calculated through a first order Taylor expansion. The standard deviations for the different parameters/variables are shown in Table 2.1. The overall standard deviation σ_R is approximately 1.5 times larger than the between laboratory standard deviation component σ_L. The remaining component is the sum of the laboratory sample interaction σ_{LS} and the within laboratory standard deviation σ_W, and was especially large for the sulfate, sodium, and magnesium determinations. The overall standard deviation was especially large for the analysis of cadmium, nitrate nitrogen, turbidity, sulfate, chromium, organic nitrogen, copper zinc, and barium.

It was concluded that substantial differences existed between different analytical methods, especially between manual and automated methods (see appendix C). For example, the automated colorimetric COD test tended to give lower results than did the manual (Tables C-6-1 and C-6-2). On the other hand, the organic nitrogen and ammonia nitrogen values obtained with the automated colorimetric Kjeldahl method and automated colorimetric method respectively, resulted in higher readings than did the manual titrimetric method (Tables C-10-1, C-10-2, C-11-1, and C-11-2). The gravimetric sulfate method generally resulted in lower values than did the automated methylthymol blue method (Tables C-12-1 and C-12-2). The mercuric nitrate method for the chloride determination resulted in lower readings than did the automated ferricyanide method (Tables C-14-1 and C-14-2). The alkalinity determination with the manual potentiometric titration yielded higher results than did the automated pH or colorimetric method (Tables C-15-1 and C-15-2). Instrumental electrochemical methods also tended to give values that were different from those of manual colorimetric or titrimetric methods. For example, the ammonia nitrogen determination with the specific ion electrode method gave higher results than did the distillation and titration method (Tables C-11-1 and C-11-2). The chloride determination with the specific

Table 2.1. Standard Deviations for all Reporting Laboratories and for only those Reporting 3 Replicates

Parameter/ Variable	All Reporting Labs			Only Labs Reporting 3 Replicates				% Labs Omitted	%Labs Attributed Excessive Systematic Error	# Labs Required for 95% Confidence Limits
	σ_R	σ_L	$\sqrt{\sigma_{LS}^2+\sigma_W^2}$	σ_R	σ_L	σ_{LS}	σ_W			
pH	.349	.152	.315	.174	.126	.108	.052	24	34	2
ORP	123	93	80	146	126	68	30	36	36*	--
Turbidity	2.01	1.47	1.38	1.46	.97	1.09	.114	23	32	1600 (260)+
Conductivity	.464	.225	.406	.215	.124	.174	.026	21	31*	86 (14)+
Volatile Acids	1.01	.627	.789	1.16	.772	.855	.151	58	25*	410 (65)+
COD	.324	.20	.254	.267	.149	.212	.066	28	25	42 (7)+
TOC	.602	.294	.525	.51	.109	.493	.069	27	18*	140 (23)+
Total Residue	.574	.517	.249	.78	.756	.185	.062	11	21	130 (21)+
Volatile Residue	.764	.638	.42	1.10	.994	.45	.172	26	26	230 (37)+
Organic Nitrogen	1.50	1.02	1.09	1.17	.92	.671	.265	44	33	900 (140)+
Ammonia Nitrogen	.89	.923	.518	1.21	.992	.69	.110	36	20	320 (51)+
Sulfate	1.80	.603	1.69	1.71	.423	1.47	.774	61	4	1300 (210)+
Total Phosphorus	1.45	1.20	.817	1.44	1.18	.610	.563	43	30*	840 (130)+
Chloride	.923	.494	.78	.971	.548	.80	.055	30	7	340 (55)+
Alkalinity	.380	.222	.309	.450	.270	.358	.033	28	20	58 (9)+
Nitrate Nitrogen	1.98	1.50	1.30	2.25	1.78	1.32	.193	39	26	1600 (250)+
Sodium	.545	.125	.53	.583	.07	.578	.037	29	25	120 (19)+
Potassium	.661	.388	.535	.595	.399	.438	.056	17	31	170 (28)+
Calcium	.74	.642	.367	.346	.068	.336	.046	11	21	220 (35)+
Magnesium	.594	.109	.584	.665	.00	.676	.036	37	26*	140 (23)+
Barium	1.41	1.05	.935	1.76	1.22	1.19	.043	33	39	800 (130)+
Iron	.532	.281	.452	.428	.234	.354	.053	32	21	110 (18)+
Zinc	1.35	1.03	.878	1.20	.889	.797	.103	31	21	730 (120)+
Lead	.962	.648	.711	1.09	.817	.644	.308	30	26	370 (60)+
Chromium	1.71	1.32	1.10	1.74	1.44	.727	.665	35	35*	1200 (190)+
Cadmium	2.16	1.78	1.23	2.58	2.32	.440	1.04	37	33	1900 (300)+
Copper	1.42	1.14	.841	1.76	1.53	.832	.251	28	24*	800 (130)+
Nickel	1.08	.732	.790	1.41	1.07	.842	.365	32	25	470 (75)+

* Similar analytical results of laboratories using different methods indicate no systematic differences between methods

+ Ranging from 90% to 110% of their averaged results (from 75% to 125%)

ion electrode gave higher results than did the mercuric nitrate method (Tables C-14-1 and C-14-2). The nitrate electrode method had a larger variation than did the cadmium reduction method (Tables C-16-1 and C-16-2).

Further, it was concluded that colorimetric methods tended to give values that were sometimes different from those of physical methods. For example, the sulfate determination with the colorimetric barium chloranilate method tended to give higher results than did the gravimetric method (Tables C-12-1 and C-12-2). On the other hand, the titrimetric/colorimetric EDTA method for the calcium determination gave lower results than did the atomic absorption method (Tables C-19-1 and C-19-2). The iron determination with the automated bipyridine method tended to give higher results than did the atomic absorption spectrophotometric method (Tables C-22-1 and C-22-2). The colorimetric phenanthroline method, on the other hand, gave lower iron values than did the atomic absorption method. Differences also exist among instrumental methods. For example, the barium determination with flame emission method tended to give higher results than did the atomic absorption method (Tables C-21-1 and C-21-2). The zinc determination with the atomic absorption graphite method tended to give higher results than did the direct aspiration atomic absorption method (Tables C-23-1 and C-23-2). On the other hand, the lead, chromium, nickel, and cadmium concentrations as determined with the graphite method tended to be lower than those of the direct aspiration method (Tables C-24-1, C-25-1, C-28-1, and C-26-1).

It was concluded that pre-testing storage time had a relatively small effect on the variation of the analytical results. A linear regression line, of the form average parameter = $a + b \cdot \text{time}$, was fitted to the average values reported by each laboratory for each test. Using a onesided t test at the 5% significance level, there was generally no significant time effect (i.e., $b < o$). The presence of outliers may have affected the results in some instances when no actual time effect existed.

The dilution effect was investigated in like manner. A regression line of the form average parameter = $a + b \cdot \log 10$ dilution, was calculated for each leachate sample. Only a few of the 10 regressions were significant (i.e. $b > o$ by one sided t test) at the 5% significance level, indicating that the particular dilutions used did not have a major effect on the outcome of the analysis.

Finally, leachate commonly differs from water and wastewater in composition and higher concentrations, which could cause interferences. Table 2.2 shows the precision comparison for the parameters in the present study and, by method, in EPA Methods for Chemical Analysis of Water and Wastes (1974), ASTM Part 31: Water (1975), and Standard Methods (1971).

Table 2.2. Precision Comparison

Parameter/ Variable	Present Study		Method	EPA (1974)		ASTM (1975)		Standard Methods	
	σ_R (%)	σ_W (%)		σ (%)	Conc. (mg/l)	σ (%)	Conc.	σ (%)	Conc.
pH	34.9	5.2	Electrometric	1.6-3.1	8.0-3.5	--	--	--	--
ORP	123 mV	30 mV	Electrometric	--	--	5-10mV	--	--	--
Turbidity	201	11.4	Photometric	1.6-26	26-180	--	--	--	--
Conductivity	46.4	2.6	Electrometric	7 -8.2	100-1710	≤ 1	--	8.6-7.8	147.0-303.0
Volatile Acids	101	15.1	Chromatographic	--	--	--	--	--	--
COD	32.4	6.6	Manual reflux	6.58	270	± 13 mg/l	--	6.5	160
TOC	60.2	6.9	IR detection	80-7.8	4.9-107	4.2-3.2	2-150	5-10	--
Total Residue	57.4	6.2	Gravimetric	--	--	--	--	5-9.7	134
Volatile Residue	76.4	17.2	Gravimetric	--	--	--	--	6.5	170
Organic Nitrogen	150	26.5	Kjeldahl N	99-26	.20-4.61	--	--	--	--
			Automated Phenate	24.6-31.8	1.89-5.81	--	--	--	--
Ammonia Nitrogen	89.0	11.0	Distillation	58-14.5	.21-1.92	--	--	69.8-21.6	.2-1.5
			Selected Ion Electrodes	3.8-2.2	1.00-.13	--	--	--	--
			Automated Phenote	.35-1.1	1.41-.43	--	--	--	--
			Direct Nesslerization	--	--	--	--	38.1-11.6	.2-1.5
			Direct Phenote	--	--	--	--	39.2-26.0	.2-1.5
Sulfate	180	77.4	Turbidimetric	26.7-5.9	9.6-199	5	--	9.1	259
			Automated Chloranilate	.3-1.5	38-294	--	--	--	--
			Gravimetric	--	--	10	20-100	4.7	259
Total Phosphorus	145	56.3	Automated Ascorbic Acid	47.2-22	.04-.30	--	--	--	--
			Manual Ascorbic Acid	30-14.5	.11-982	--	--	--	--
Chloride	92.3	5.5	Mercuric Nitrate	9.06-2.96	17-398	45.3-2.7	1-100	3.3	2.41
			Ferricyanide	--	--	0-5.6	.035-10	--	--
			Argentometric	--	--	--	--	4.2	2.41

Table 2.2 Precision Comparison (continued)

Parameter/ Variable	Present Study		Method	EPA (1974)		ASTM (1975)		Standard Methods	
	σR (%)	σW (%)		σ (%)	Conc. (mg/1)	σ (%)	Conc.	σ (%)	Conc.
Alkalinity	38.0	3.3	Potenti	15-8-4.0	8-119	--	--	1 mg/1	--
Nitrate Nitrogen	198	19.3	Automated Cadmium Reduction	4.1-26.3	.29-2.48	--	--	0.0-20	.1-2.1
			Manual Cadmium Reduction	--	--	--	--	96.5-9.2	.05-5
			Brucine	57.5-17.3	.16-1.24	--	--	66.7-15.4	.05-5
Sodium	54.5	3.7	Flame Photometric	--	--	65.1-1.7	1-100	17.3	19.9
			Direct A.A.	1.5	8.2-52	--	--	--	--
Potassium	66.1	5.6	Flame Photometric	--	--	45.9-1.35	1-100	15.5	3.1
			Direct A.A.	10.3-10.2	1.6-6.3	--	--	--	--
Calcium	74	4.6	EDTA Titrimetric	--	--	--	--	9.2	108
			Direct A.A.	.3-.6	9.0-36.0	20.3-7.3	.3-15	--	--
Magnesium	59.4	3.6	Direct A.A.	4.76-2.5	2.1-8.2	67.8-8.7	.05-3.5	10.5	2
Barium	141	43.1	Direct A.A.	10.8-6.5	.40-2.0	--	--	10	.5
Iron	53.2	5.3	Direct A.A.	609-21	.01-.84	56-6.25	.1-20	16.5	.3
			Phenanthroline	--	--	--	--	25.5	.3
Zinc	135	10.3	--	314-34.5	.007-.281	55-5.3	.02-3	8.2	.5
Lead	96.2	30.8	--	114-33	.025-.334	57-7.4	.34-40	23.5	.05
Chromium	171	66.5	--	105-28.4	.007-370	29.4-9.6	.2-20	26.4	.05
Cadmium	216	104	--	350-23	.0014-.078	0-8.7	.22-5	21.6-43.8	.05
Copper	108	36.5	--	81-17	.0075-.332	33.8-3.95	.1-20	11.2	1
Nickel	142	25.1	--	5.5-.8	.2-5.0	52.4-2.6	.08-20	--	--

SECTION 3

RECOMMENDATIONS

RESEARCH RECOMMENDATIONS

Based on the results of the present study it is recommended that a within laboratory study using the standard addition technique should be used to evaluate the automated COD test, automated Kjeldahl test, automated methylthymol blue sulfate method, and automated alkalinity test. Electrochemical methods that need further testing are the specific ammonia electrode, chloride electrode, and nitrate electrode. Further research is required to determine the systematic differences between the atomic absorption direct aspiration and graphite furnace method.

The current analysis of the leachate data has been done only on the data as reported; the data should be processed for outliers between replicates and between laboratory means using one of several statistical techniques. The analysis of variance should then be repeated on these remaining data. The present study showed that the largest portion of the overall variation was usually due to a sample laboratory interaction. It is recommended that further statistical analysis be conducted using the existing or expanded data base to determine whether this interaction term is more strongly present in certain leachate samples than in others. The same analysis will determine whether certain laboratories are more subject to this interaction than are other laboratories.

ANALYSIS RECOMMENDATION

pH

It is recommended that the pH be determined with the electrometric method using the glass electrode and temperature correction. The analysis should be conducted on a freshly collected sample as CO_2 evolution and metal hydroxide precipitates will effect this parameter. The method has a high precision compared with the other parameters. In conjunction with the conductivity determination it serves as an indicator for the presence of leachate in groundwater. Both measurements can be made in a short time period and most laboratories include it in their routine testing. Values between 4 to 6 generally correspond with high free volatile fatty concentrations.

acid

ORP

It is recommended that the ORP be determined with the electrometric method using the platinum electrode with the calomel reference electrode.

The analysis should be conducted on a freshly collected leachate sample as gradual oxidation due to atmospheric exposure will increase the value of this parameter. The method has an intermediate precision compared with the other parameters. A significant number of laboratories are not able to perform this analysis satisfactorily. It serves as an indicator of the degree of anaerobiosis of the sample. Values between -200 to -100 mv generally correspond with low pH values, while values above -100 mv can reflect atmospheric exposure or oxiding conditions.

Turbidity

It is recommended that the turbidity be determined with the nephelometric method and not with the visual Jackson turbidity method as the latter method tends to give higher readings. The analysis should be conducted on a freshly collected sample as formation of hydroxide precipitated will cause the value to increase. The method has a low precision compared with the other parameters and should be substituted by a suspended solids determination. Values above 500 mg/l generally reflect high iron concentrations and oxidizing conditions.

Conductivity

It is recommended that the conductivity be determined with the electrometric method using the platinum electrode and temperature correction. The method has a high precision compared with the other parameters. It is a good indicator for the presence of leachate. The measurement can be made in a short time period and most laboratories include it in their routine testing. The parameter reflects the presence of both inorganics and organic fatty acids. A pH increase of the sample generally results in higher conductivity values due to further ionization of the fatty acids. Values above 2500 micromhos/cm often reflect the presence of concentrated leachate. High strength leachate generally has a COD/conductivity ratio greater than 1.0 while leachate from older fills often has a lower ratio.

Fatty Acids

It is recommended that the free volatile fatty acids be done with the partition chromatographic method as this has superseded the earlier distillation and titration method. The method has a relatively low precision while it is time consuming. The majority of evaluated laboratories were not able to perform the analysis satisfactorily. The analysis should be conducted together with an organic parameter of higher precision such as COD. With carefully controlled conditions the method can detect concentrations above 50 mg/l. Values of the fatty acid/COD ratio above 0.4 reflect a concentrated leachate undergoing active anaerobic decomposition. Lower values of the ratio often reflect a stabilized leachate from older fills. The ratio becomes a less reliable indicator at low concentration levels.

Chemical Oxygen Demand

It is recommended that the chemical oxygen demand be determined with the manual dichromatic reflux method using the ferrous ammonium sulfate titration. The analysis should not be done with the automated dichromate method with the colorimetric measurement of the reduced dichromate as systematically low results may be obtained. The method has the highest precision of any of the parameters tested and is a good indicator of the general organic strength of the leachate. While the between laboratory evaluation did not detect a significant time effect, a within laboratory study showed a decrease in COD value after 2 days of storage and the analysis should therefore be conducted within a 2 day time period. Results above 1 mg/l should be reported. When conducted together with other parameters high strength leachate generally has a BOD/COD ratio above 0.5, a conductivity/COD ratio above 1, a fatty acid/COD ratio above 0.4, and a COD/TOC ratio above 2.5. Lower values are often obtained in more stabilized leachates from older landfills.

Total Residue

It is recommended that the total residue be determined with the 104°C drying method and not with the 180°C drying method. The analysis reflects the presence of organics and inorganics and has a moderate precision comparable to the TOC analysis. More laboratories are able to perform this analysis satisfactory than any other method. Results should be reported above 10 mg/l. The test should be conducted together with the conductivity. Common total residue/conductivity ratios observed in high strength leachate are above 1.0 while stabilized leachates from older fills often have ratios below 0.5.

Volatile Residue

It is recommended that the volatile residue be determined at 550°C and that prior filtration of the sample not be utilized as lower results are obtained. Hydroxide formation in the sample likely causes the precipitation of organics which are subsequently removed during filtration of the suspended solids. Results should be reported above 10 mg/l. The analysis should be conducted concurrently with the total residue determination. The analysis reflects the presence of organics in leachate but has a lower precision than the COD or TOC test. The ratio of volatile residue to total residue can be as high as 0.5 in high strength leachate but will decrease to lower values for stabilized leachate from older landfills. The ratio of volatile residue to COD can be as high as 1.0 in high strength leachate. This ratio becomes more variable in stablilized leachate as volatilization of carbonates may contribute to relatively high values.

Organic Nitrogen

It is recommended that the organic nitrogen be determined with the Kjeldahl manual titration method and not with the automated Kjeldahl phenate colorimetric method as the latter tends to give higher values. Analytical results should be reported above 0.1 mg/l. The precision is lowest of all organic parameters that were evaluated. Relatively few laboratories determine this parameter in leachate and a large number produce unacceptable results. The parameter should be determined concurrently with the ammonia nitrogen test. The nitrogen determination is required to determine the need for nutrient supplements during aerobic biological treatment of leachate. High strength leachates sometimes have TOC/org^{N} ratios above 20 while it is often below 10 for stabilized leachates from old fills. Degradation of organic nitrogen will result in the formation of nitrate which has a maximum concentration limit (MCL) in the drinking water standards.

Ammonia Nitrogen

It is recommended that the ammonia nitrogen be determined with the distillation titration method and not with the distillation Nesslerization method as the latter gives higher results. The automated colorimetric phenate method and the specific ion electrode also tended to give higher results. Analytical results should be reported above 0.1. The precision is less than observed for the other major cations and a significant number of laboratories are not able to perform a satisfactory analysis. The recovery of the spiked leachate sample for this parameter was relatively high and care should be exercised that extraneous influences are excluded during the analysis. The value of the parameter will increase during storage of the sample due to the organic nitrogen degradation. The ammonia analysis should therefore be conducted in conjunction with the organic nitrogen analysis. The ratio of ammonia to organic nitrogen commonly ranges from 0.5 to 2.

Sulfate

It is recommended that the sulfate analysis be conducted with the gravimetric method and not with the automated methyl thymol blue method as higher results are obtained with the latter method. The manual and automated turbidimetric method should not be used due to possible interference by suspended particles in leachate. The colorimetric chloranilate method also tends to give higher results. Analytical results should be reported above 0.5 mg/l. The precision is relatively low in comparison with the other anions and relatively few laboratories determined this parameter in leachate. The majority of the laboratories produce unacceptable results for this test. Under reducing conditions sulfur will precipitate heavy metals as sulfides.

Phosphorus

It is recommended that the total phosphorus analysis be conducted with the ascorbic acid method using the persulfate digestion step and not with the stannous chloride method as the latter gives slightly lower results, possibly due to Fe, Ca and Na influence. Analytical results should be reported above 0.05 mg/l. Compared with the other anions it has an intermediate precision. A large number of laboratories are not able to perform the analysis satisfactorily. The recovery of phosphorus in the spiked leachate sample was negative, possibly due to formation of a precipitate. Common N/P ratio around 30 are often seen in high strength leachate and P often has to be added to leachate as a nutrient during aerobic biological treatment.

Chloride

It is recommended that the chloride analysis be conducted with the potentiometric titration method and not using the direct readings of the specific ion electrode. The argentrometric and automated ferricyanide methods should not be used as they tend to give higher results due to interfering substances. Analytical results should be reported above 0.5 mg/l. The method has a relative high precision and most laboratories are able to perform the test satisfactory. The parameter does not have a major interaction with the soil complex during its migration and therefore serves as a good indicator for the presence of leachate.

Alkalinity

It is recommended that the alkalinity determination be conducted with the potentiometric method with titration to the inflection point around pH 4.5 and not with the automated pH or colorimetric method as relatively low results are obtained with the latter methods. The method has the highest precision of all anionic methods and results should be reported above 1 mg/l. In high strength leachate fatty acids enhanced the determination while in stabilized leachate it reflects the presence of bicarbonates.

Nitrate Nitrogen

It is recommended that the nitrate determination be conducted with the cadmium reduction method after separate determination of the nitrite ion. The zinc reduction, brucine and specific ion electrode should not be used as these methods tend to give higher results. The method has the lowest precision of all anionic methods and a significant number of laboratories produce unacceptable results. Analytical results should be reported above 0.01 mg/l. The recovery in a spiked leachate sample was negative, possibly due to denitrification. This parameter is not likely to be present under anaerobic conditions in high strength leachate but will be present in significant quantities in stabilized leachate. The parameter should be determined in conjunction with the ammonia. Nitrate is listed as a MCL in the drinking water standards.

Sodium and Potassium

It is recommended that the sodium and potassium determination be conducted with the atomic absorption or manual flame or automated flame emission method. The graphite method or flameless emission method should not be used as they result in relatively low values. Both the emission and absorption methods have a relatively high precision and these parameters are commonly determined. Very few laboratories are not able to perform this analysis satisfactory. Analytical results should be reported above 0.1 mg/l. Cesium nitrate should be added to the sample to suppress the ionization when both are determined with the atomic absorption method. During stabilization of leachate with increasing age of the fill sodium and potassium retain relatively high concentrations with respect to other cations. During passage through soil sodium is exchanged against calcium which is the basis for the calcium halo affect around landfills.

Calcium, Magnesium, Barium

It is recommended that the calcium, magnesium and barium analysis be conducted with the atomic absorption spectrophotometric method and not with the EDTA titration method or graphite furnace as these give higher and lower results respectively. Analytical results for all three cations should be reported above 0.1 mg/l. The former two cations have precisions comparable to sodium and potassium while the precision for barium is twice as low. Trivalent lanthanum should be added as releasing agent to suppress sodium and potassium enhanced readings. Calcium and magnesium analysis should use an air-acetylene flame while barium should be measured with a nitrous oxide acetylene flame. Drinking water standards allow a MCL of 1.0 mg/l for BA.

Heavy Metals (Fe, Zn, Pb, Cr, Cd, Cu, Ni)

It is recommended that the heavy metal be conducted with the direct aspiration atomic absorption spectrophotometric method and not with the AA graphite or colorimetric method. The AA graphite method generally gave lower results than the direct aspiration method except for copper. The lowest precision was observed for cadmium while the highest precision was found for iron, inversely related to their detection limits. The detection limits for the direct aspiration method was 3-10 times below the drinking water MCL and it therefore satisfactory. Negative recoveries were noted in the spiked sample for lead and iron possibly due to absorption and precipitation reactions.

SECTION 4

DATA BASE

Of the 120 laboratories initially contacted 52 (6 of them in Canada) indicated willingness to participate in the round robin study and to determine approximately 80% of the requested 28 parameters. Twenty percent were university laboratories, 20% commercial laboratories, and 60% state and federal laboratories.

Ten 120ℓ (30 gallon) leachate samples were collected in 20 (5 gallon) containers, from the 9 locations listed in Table 4.1. All samples were collected, chilled, and stored anaerobically. The samples were immediately transported by air to Stanford University where each sample was emptied anaerobically into a 150ℓ vessel, thoroughly mixed, placed in 55 1ℓ glass containers and 110 500 ml polyethylene containers, and chilled for distribution by airfreight to the participating laboratories. After complete mixing of the two Illinois samples, half was spiked with each of the chemical constituants to concentrations about 25% those in the unspiked sample. Each laboratory received instructions for sample handling, sequence of analysis, and reporting analytical results.

Thirty-two laboratories actively submited final analytical results. The return rate for laboratories reporting results for specific tests ranged from 42% to 66% (see Table 4.2).

Most measured COD concentrations were close to the estimated values, indicating that the latter greatly aided in selection of the optimum dilution factor. The largest deviation between the estimated and measured values was noted for Enfield, Connecticut, which was 15 times more dilute than expected. In all, the values covered a wide concentration range from a high of 27,284 mg/ℓ to a low of 98 mg/ℓ.

The participating laboratories recorded information on Standard Reporting Forms (SRF's), a sample of which is shown in Figure 4.1. The amount of information reported was variable; missing information made the coding of the data base and the checking of arithmetic computations difficult. For example, several laboratories had a blank reading that was higher than that for other laboratories, but information to explain different values was lacking.

TABLE 4.1. LEACHATE COLLECTION LOCATIONS AND INITIAL ANALYTICAL RESULTS

Location	Well/Drain	Symbols	Estimated COD (mg/ℓ)	Measured COD (mg/ℓ)
Center Hill, Cincinnati, Ohio	Lysimeter Cell 16 Chlorine Brine Drainpipe	A	30,000	27,284
Enfield, Connecticut	Groundwater Well 26	B	30,000	2,168
Tellytown, Pennsylvania	Combined leachate Influent	C	23,000	16,084
Llangollen, Delaware	Groundwater Well S 1	D	10,000	10,719
Univ. of Illinois, Urbana, Illinois	Lysimeter Drainpipe (spiked)	E	7,500	3,408
Univ. of Illinois, Urbana, Illinois	Lysimeter Drainpipe	F	5,000	2,047
Boon County, Kentucky	Test Cell Upper Drainpipe	G	3,000	945
Univ. of British Columbia, Vancouver, British Columbia	Lysimeter Cell K Drainpipe	H	1,800	1,298
Sonoma County, California	Test Cell D Recycle Drainpipe	I	700	423
Dade County, Miami, Florida	Groundwater Well 4-20	J	100	98

FIGURE 4.1 STANDARD REPORTING FORM

Designated Laboratory Number

Sample Number

Analysis

Method selected

Principal reagents

Equipment

Name of chemist conducting the analysis

Date of sample arrival

Date of analysis

Equation used to calculate final concentration

Dilutions used

Volume of diluted sample (if appropriate)

Reading obtained for first aliquot _____; calculated concentration_____ mg/l*

Reading obtained for second aliquot _____; calculated concentration _____ mg/l*

Reading obtained for third aliquot _____; calculated concentration _____ mg/l*

Reading obtained for blank (if appropriate) ______

Calculated average concentration

Visual observation regarding test before and during analysis:

Please Return to:
Dr. Foppe B. DeWalle
Department of Civil Engineering
Stanford University
Stanford, CA 94305

*Report as many significant figures as you can confidently report; do not round off.

TABLE 4.2. PERCENTAGE OF LABORATORIES REPORTING DATA

Parameter	Number of Laboratories Reporting	Total Number of Laboratories	Percent Returns (%)
pH	29	49	59
ORP	11	18	61
Turbidity	22	39	56
Conductivity	29	45	64
Volatile Acids	12	20	60
COD	25	46	54
TOC	22	34	65
Total Residue	28	45	62
Volatile Residue	27	41	66
Organic Nitrogen	18	38	47
Ammonia Nitrogen	25	46	54
Sulfate	23	44	52
Total Phosphorus	23	43	53
Chloride	27	49	55
Alkalinity	25	45	56
Nitrate-Nitrogen	23	45	51
Sodium	28	46	61
Potassium	29	44	66
Calcium	28	46	61
Magnesium	27	46	59
Barium	18	43	42
Iron	28	49	57
Zinc	29	49	59
Lead	27	49	55
Chromium	28	49	57
Cadmium	27	48	55
Copper	29	48	60
Nickel	28	48	58

The SRF's were manually edited to prepare them for keypunching. Numeric codes were established for the laboratory, leachate sample, parameter analyzed, and, with difficulty, for the method, reagents, and equipment used. The number -1 was used as a missing information indicator except in coding the method used for some parameters. Incompleteness and inconsistencies on the SRF's for methods, reagents, and equipment could have been better handled by establishing codes prior to the analyses. The date, dilution factor, volume of sample, the three replicates, blank reading, and the number of replicates were uniformly edited as follows.

If replicate determinations of a leachate sample were performed on different dates, the average date was used in the data base. This situation occurred infrequently.

If dilution ratios were given by a specific laboratory for some of the leachate samples, but omitted for the remaining samples, it was assumed that no dilution was actually used. If more than one dilution was used for the replicate values of a given leachate sample, the average dilution was used in the data base. This situation occurred very infrequently. There appears to be inconsistency in the shorthand notation often used for reporting dilutions. For example, 1:1 can mean that either no dilution was used, or 1 unit of sample was diluted to 2 units total. In most instances when 1:1 was reported, it was recorded as a dilution factor of 2 in the data base.

It was indicated on the SRF to report as many significant figures as could be confidently reported for concentration values. In the data base three significant figures were retained except for numbers greater than 10^3 where all reported non-decimal digits were retained. When a value was reported in the form of a detection limit (i.e., < value), half of this value was used for all statistical analyses.

The data were processed using a program that checked the consistency of the laboratory, parameter, method, reagent, equipment, and the number of replicates code numbers, the sequence of the leachate sample code numbers, and structural features incorporated to facilitate the management of the data base. The data were not checked to see if reported values occurred within a reasonable range.

SECTION 5

DATA PROCESSING

All major computation and data file management were performed on the Control Data Cyber 173 and CDC 6400 dual mainframe system of the Academic Computer Center at the University of Washington. The leachate data base was maintained on disc and magnetic tape files. Most of the data preprocessing programs used for data sorting and the computation of sample statistics were written in FORTRAN, compiled with the University of Minnesota Fortran compiler (Version 5.1), and executed under the CDC NOS/BE (Version 1.2) operating system. The statistical package Minitab II (Ryan et al., 1976) was used extensively in the statistical analysis and plotting of the leachate data. Hand calculators were used for simple computations and to verify the results of computer programs. The reported concentration levels were processed with a G12.5 format specification for all 28 parameters. A G13.6 format specification was used for the average and standard deviation computed for the concentration levels.

Special mention should be made of the plotting symbols used in all printer plots. The plotting symbols A through J were used to represent data for the leachate sample of the same letter. When two or more values were plotted at the same printer character position, the symbols 2 through 9 indicate the number of values plotted, and a + indicates ten or more values plotted.

SECTION 6

STATISTICAL DESIGN

The statistical techniques used for analyzing the leachate data are described and the interpretation of the results is discussed in this section. Alternate statistical techniques are mentioned where they would be appropriate for more detailed analyses of the leachate data.

The interpretation and computational aspects in the statistical analysis of data become more difficult as the data become unbalanced for example, when three replicates were not given or when all ten samples were not analyzed. These difficulties are hard to deal with when the analysis of variance is used to analyze data having a factorial treatment design where the factors are considered as random effects (i.e., variance component models). To have ensured a balanced data set, the instructions for data collection should have more strongly stated that three replications per sample per parameter were required. The data from laboratories reporting three replicates for all ten leachate samples were used to form a balanced data set and were used for some of the statistical analyses. The average values computed for each laboratory were also used to form a balanced data set which was used for most of the analyses performed.

The data from each parameter were analyzed using the following approach. The within and between laboratory standard deviations were plotted against the concentration level to determine if a transformation of the data was required to make the variability at different levels of the parameter approximately equal. Quantile-quantile plots were then constructed for the original and transformed data, and used to determine if the distributions of the original or the transformed data were reasonably close to a normal distribution. To determine if systematic differences exist between the analytical methods used and between laboratories, a ranking procedure was used. Finally, the analysis of variance was used to estimate the between laboratory, laboratory sample interaction, and within laboratory variance components.

COMPUTATION OF AVERAGES - UNWEIGHTED AND WEIGHTED

Let X_{ijk} be the value of the k^{th} replicate, $k=1, \ldots, n_i$, from the i^{th} laboratory, $i=1, \ldots, m$, for the j^{th} sample. The variance component model used to model these values reported by the laboratories is

$$X_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \varepsilon_{ijk},$$

where α, β, and γ represent laboratory, sample and lab sample interaction effects, respectively. The term ε represents random error between replicates within a single laboratory. It is assumed that these terms act independently of each other, have zero means, and variances $\sigma^2{}_L$, $\sigma^2{}_S$, $\sigma^2{}_{LS}$, and $\sigma^2{}_W$ respectively. The term μ represents a constant mean term.

If we are concerned only with analyzing a particular leachate sample, then the j^{th} subscript will remain constant and can be dropped from the model. The reduced model becomes

$$X_{ik} = \mu + \alpha_i + \beta + \gamma_i + \varepsilon_{ik}$$

$$= \mu' + \delta_i + \varepsilon_{ik},$$

where $\mu' = \mu + \beta$, and $\delta_i = \alpha_i + \gamma_i$.

The expected value and variance of X_{ik} are μ' and $\sigma^2{}_L + \sigma^2{}_{LS} + \sigma^2{}_W$ respectively. The covariance between X_{ik} and $X_{i'k'}$ is $\sigma^2{}_L + \sigma^2{}_{LS}$ for $i = i'$ and $k \neq k'$, and 0 for $i \neq i'$.

If we have results from m laboratories with each laboratory performing n_i replicates on a particular leachate sample, how should we average these results to estimate the concentration μ' of the sample?

Define an unweighted average of the X_{ik} to be

$$\overline{X}_U = \frac{1}{m} \sum_i \overline{X}_{i.} = \frac{1}{m} \sum_i \frac{1}{n_i} \sum_k X_{ik},$$

where $\overline{X}_{i.} = \frac{1}{n_i} \sum_k X_{ik}$.

The summations over index i are for $i=1, \ldots, m$, and the summations over index k are for $k=1, \ldots, n_i$.

The expected value of $\overline{X}_U$ is μ' (i.e., unbiased for μ') and

$$\text{Var } \overline{X}_U = \frac{1}{m} (\sigma^2{}_L + \sigma^2{}_{LS}) + \frac{1}{m^2} \sum_i \frac{1}{n_i} \sigma^2{}_W .$$

Note that $\overline{X}_U$ is unweighted in the sense that each laboratory average receives the same weighting.

Define a weighted average of the X_{ik} to be

$$\overline{X}_W = \frac{1}{\sum_i n_i} \sum_i n_i \, \overline{X}_{i.} + \frac{1}{\sum_i n_i} \sum_i \sum_k X_{ik},$$

where $\overline{X}_{i.} = \frac{1}{n_i} \sum_k X_{ik}$.

The expected value of $\overline{X}_W$ is μ'(i.e. unbiased for μ') and

$$\text{Var } \overline{X}_W = \frac{\sum_i n_i^2}{(\sum_i n_i)^2} (\sigma^2_L + \sigma^2_{LS}) + \frac{1}{\sum_i n_i} \sigma^2_W.$$

Note that $\overline{X}_W$ is weighted in the sense that each laboratory average is weighted in proportion to the number of replicates n_i done by that laboratory.

As both $\overline{X}_W$ and $\overline{X}_U$ are unbiased estimators for μ', the one with the smallest variance will be the preferred estimator for the concentration of the sample μ'. A term by term ($\sigma^2_L + \sigma^2_{LS}$ and σ^2_W) comparison of the variances of $\overline{X}_W$ and $\overline{X}_U$ (using the Cauchy-Swartz inequality) shows that neither estimator has the smallest variance under all conditions.

The following result has not been derived rigorously and thus should be used with caution. It appears that the Var $\overline{X}_W >$ Var $\overline{X}_U$ when $\sigma^2_L + \sigma^2_{LS} > \sigma^2_W$ and thus $\overline{X}_U$ would be preferred over $\overline{X}_W$. Using this result combined with estimates of $\sigma^2_L + \sigma^2_{LS}$ and σ^2_W, from the leachate data, where $\sigma^2_L + \sigma^2_{LS}$ was typically much greater than σ^2_W it would appear that $\overline{X}_U$ would usually be the preferred estimator of the concentration level of the sample μ' for leachate data. In this report $\overline{X}_U$ was used for the calculation of the average concentrations of the leachate samples.

To avoid the above complications, if all laboratories reported the same number of replicates (i.e., $n_i = n$ for all i=1, ..., m), then $\overline{X}_W$ and $\overline{X}_U$ are equivalent. Let $\overline{X} = \overline{X}_W = \overline{X}_U$ in this case and here

$$\overline{X} = \frac{1}{mn} \sum_i \sum_k X_{ik} \, .$$

The expected value of $\overline{X}$ is μ' (i.e. unbiased for μ') and

$$\text{Var } \overline{X} = \frac{\sigma^2_L + \sigma^2_{LS}}{m} + \frac{\sigma^2_W}{mn} \, .$$

DISTRIBUTION OF THE DATA

To determine if the homogeneity of variance assumptions required by the analysis of variance technique used to provide variance component estimates are reasonably satisfied, the relationship of the within and between laboratory standard deviation with the level of the parameter was investigated.

For each leachate sample a within laboratory standard deviation was calculated by pooling the standard deviations computed from the replicates of each laboratory. The formula used was

$$S = \sqrt{\Sigma(n_i-1)S_i{}^2/\Sigma(n_i-1)}$$

where n_i is the number of replicates from the i^{th} laboratory and $S_i{}^2$ is the variance computed from the replicates of the i^{th} laboratory. A standard deviation can not be computed for those laboratories that reported only an average value or only one replicate. Also for each sample a sample average was computed by taking the average of the laboratory averages, but excluding those laboratories that reported only an average value or only one replicate. A plot was made of these values and a simple linear regression equation calculated.

If a relation between the standard deviation and the mean of the form $\sigma = a\ \mu^b$ is assumed, by taking logs we obtain $\log \sigma = \log a + b \log \mu$. The logarithms of the sample values for these parameters were plotted against each other and a simple linear regression equation was calculated. A 95% confidence interval for the estimated power (b) to which μ is raised (i.e., the coefficient of $\log \mu$) was computed. If the amount of variability explained by the regression lines was reasonably high (i.e., high R^2 values), the value of b was used to determine the required variance stabilizing transformation. If the computed confidence interval for b included the value 1, then a logarithmic transformation is indicated. If the value .5 is included, then a square root transformation is indicated.

A between laboratory standard deviation was computed for each leachate sample from the laboratory averages. The grand sample average was computed for each leachate sample by taking the average of the laboratory averages. All of the laboratories are included for these computations except when a laboratory did not report any results for a particular sample. A plot was made of these values and a regression equation calculated. As was done for the within laboratory standard deviation, the logarithms of these values were plotted, a regression equation calculated, and the required variance stabilizing transformation was determined.

When the logarithmic transformation was indicated to stabilize the within and between laboratory variances, the $\log_e$ transformation was applied to each replicate, and the statistical analyses are performed on these transformed data.

The within and between laboratory standard deviations and the grand sample averages given in the analytical results summary tables of the measured parameters were calculated using the procedures just stated.

If a natural logarithmic (base e) transformation is used, the following relationship is also of interest. The standard deviation of the data in the transformed scale is approximately equal to the coefficient of variation of the data in the original scale of measurement. This is true regardless of the actual distribution appropriate for the original scale. This relationship is derived by using a first order Taylor expansion of the $\log_e$ transformation and computing the mean and variance based on this expansion. This approximation is reasonably good provided that the coefficient of variation in the original scale is small.

An example of the logarithmic transformation for the lognormal distribuiton follows. If the lognormal distribution is adequate to model data obtained in a certain scale of measurement, then applying the $\log_e$ transformation will have the following effect. The transformed data will be distributed as a normal distribution having mean m and variance v^2. The mean, variance and coefficient of variation in the original scale are $\exp(m+v^2/2)$, $\exp(2m+v^2)[\exp(v^2)-1]$, and $\sqrt{\exp(v^2)-1}$ respectively. For the lognormal distribution the standard deviation is a function of the mean of the form $\sigma = a\mu$ where $a = \sqrt{\exp(v^2)-1}$, the coefficient of variation. That the standard deviation v in the transformed scale is approximately equal to the coefficient of variation $\sqrt{\exp(v^2)-1}$ in the original scale for small values of the latter can be seen in Table 6.1. For the lognormal distribution a coefficient of variation of .5 or less could be considered small with regard to the adequacy of the Taylor expansion approximation just discussed.

The within laboratory and between laboratory standard deviations and the grand sample averages given in the analytical results summary tables of the measured parameters were calculated using the above stated procedures.

TABLE 6.1. ACCURACY OF COEFFICIENT OF VARIATION APPROXIMATION

$\sqrt{\exp(v^2)-1}$	v	$v/\sqrt{\exp(v^2)-1}$
.01	.009999+	.9999+
.05	.04997	.9994
.1	.09975	.9975
.25	.2462	.9849
.5	.4724	.9448
1.0	.8326	.8326
1.5	1.0857	.7238
2.0	1.2686	.6343

Quantile-quantile plots were used to determine if the distributions of the original data or the transformed data were reasonably close to a normal distribution. The ordered laboratory averages for the original and transformed data were plotted against the quantiles from a normal distribution for the ten leachate samples A through J. Linear regression equations were calculated for each sample for both the original and transformed data.

If the distribution of the data were normal, then the quantile-quantile plots would appear close to a straight line relationship. The R^2 values of the computed regression equations were used as a measure of how close the actual distributions of the data were to a normal distribution. Outlying averages are reasonably apparent in these plots. The R^2 values of the regression equations computed for both the original and transformed data can be greatly affected by outlying averages however.

ANALYTICAL METHODS COMPARISON AND LABORATORY RANKING

When more than one method was used in the determination of a parameter, a three way classification analysis of variance would be the preferred technique to determine if systematic differences exist between the methods. This was not done as the number of laboratories performing different methods was usually very unbalanced. A simple nonparametric test applicable to two way classified data without interaction, the Friedman test, was used to determine if the laboratories have identical performance (Conover, 1971).

The Friedman test consists of ranking the laboratories based on the average reported value for each leachate sample. The lowest value within each leachate sample is assigned the rank of 1, the second lowest, the rank of 2,..., and so on. These ranks are summed over the leachate samples for each laboratory. If an average value for a laboratory was missing for a particular sample, it was replaced by the average of the values reported for that leachate sample by the other laboratories. The hypothesis that the laboratories have identical performance can be tested using a function of the rank sums scored by the laboratories which has an approximate chi square distribution. Excessive systematic error is attributed to those laboratories scoring low or high rank sums. Extreme rank sum scores were determined by extending the tabulated values given in Thompson and Wilke (1963). The results obtained by the ranking procedure are not conclusive however, as any method effects are confounded with laboratory effects.

The rank sums scored by the laboratories using different methods were arranged by increasing rank sum which provides a visual method for detecting systematic differences between the methods and also provides a comparison of the relative variability of the methods. The methods comparison provided by the rank sums is supported by graphs of the laboratory averages plotted against the methods that were used. These plots also provide a comparison of the relative variability between different methods.

VARIANCE COMPONENT ESTIMATES

The analysis of variance and variance component estimation techniques used in this report are thoroughly described in many statistical textbooks. The reader who is interested in obtaining more details on the computational and interpretational aspects of those techniques is referred to Searle (1971), Winer (1971), or Steiner (1975). As the data were not processed for outliers,the resulting variance component estimates will be larger than if the data had been processed for outliers.

For the analysis of the leachate data a two way classification analysis of variance was used with laboratories and samples as factors. Both factors were considered to be random effects. As the laboratories participating in this study are not the only laboratories which do leachate analysis, considering laboratories as a random effect may be reasonable even though they are not a small, completely random sample of laboratories. The return rate of laboratories reporting results was approximately 60% however (see Section 4) which may have introduced a bias. The 10 leachate sample collection sites were selected from a list of approximately 50 sites chosen on the basis of representing different climatic conditions, varying site age, and having a wide chemical oxygen demand range. The 50 sites represent only a small number of possible solid waste landfill sites in the United States of America and Canada from which leachate samples could be collected. Considering the leachate samples as a random effect may be reasonable; however,it could be argued that they represent a fixed effect because of the partially systematic manner in which they were chosen.

The linear model used for this treatment design is

$$X_{ijk} = \mu + \alpha_i + \beta_j + \gamma_{ij} + \varepsilon_{ijk},$$

where X_{ijk} is the value of the k^{th} replicate, k=1, ..., n, from the i^{th} laboratory, i=1, ..., m, for the j^{th} leachate sample, j=1, ..., 10. The terms α, β, and γ represent laboratory, sample, and laboratory sample interaction effects, respectively. The term ε represents random error between replicates within a single laboratory. It is assumed that these terms act independently of each other, have zero means, and variances $\sigma^2{}_L$, $\sigma^2{}_S$, $\sigma^2{}_{LS}$, and $\sigma^2{}_W$ respectively. The term μ represents a constant mean term. The variance components of interest are the between laboratory ($\sigma^2{}_L$), laboratory sample interaction ($\sigma^2{}_{LS}$), and within laboratory ($\sigma^2{}_W$) components. The expected mean squares for the sources of variability of interest are given in Table 6.2. In this table let s=10 be the number of leachate samples analyzed, n is the number of replicates, and m is the number of laboratories.

TABLE 6.2. EXPECTED MEAN SQUARES

Source of Variability	Degrees of Freedom	Expected Mean Square
Laboratories	m-1	$\sigma^2_W + n\sigma^2_{LS} + ns\sigma^2_L$
Lab x Sample	(m-1)(s-1)	$\sigma^2_W + n\sigma^2_{LS}$
	ms(n-1)	σ^2_W

The estimation of variance components is discussed in detail by Searle (1971). The variance components can be estimated by forming the appropriate linear combination of mean squares. The between laboratory (σ^2_L) variance component is estimated by subtracting the mean square lab x sample from the mean square laboratories and dividing this by ns. The laboratory sample interaction (σ^2_{LS}) variance component is estimated by subtracting the mean square residual from the mean square lab x sample and dividing this by n. The within laboratory (σ^2_W) variance component is estimated by the mean square residual. These estimators are the minimum variance unbiased estimators of the variance components. The overall reproducibility (σ^2_R) is the sum of the between laboratory, laboratory sample interaction and within laboratory variance components (Steiner, 1975). A leachate matrix problem would be indicated if the laboratory sample interaction variance component was large relative to the overall reproducibility.

If only a single replicate was made (n=1), the laboratory sample interaction and within laboratory variance components cannot be estimated independently; only their sum can be estimated. The between laboratory variance component and the overall reproducibility can still be estimated in this situation. The laboratory averages were used to form a data set having this structure. All of the laboratories could be included by using this approach. It would be expected that the magnitude of the estimated variance components would be greater than the corresponding estimates obtained from the subset of laboratories having three replicates for all ten leachate samples. The main reason explaining this is that more outlying results are likely to be included as more laboratories are included in the data set being analyzed. If an average value for a laboratory was missing for a particular sample, it was replaced by the average of the values reported for that leachate sample by the other laboratories.

When the variance component estimates are computed for the $\log_e$ transformed data, the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

This is an approximate relationship which was discussed earlier. Also, the estimated coefficient of variation (c.v.) can be used to calculate the standard deviation in the original scale of measurement at a specified concentration by the formula σ = c.v. μ. This is based on the assumption that the c.v. remains constant over all concentration levels, however.

If hypothesis testing is to be done in addition to estimation, it is further required that the terms α_i, β_j, γ_{ij}, and ε_{ijk} are normally distributed. This assumption is also required to form confidence intervals for the estimated variance components. The hypothesis that the between laboratory variance component (σ^2_L) is zero can be tested by forming the F ratio of the mean square laboratories divided by the mean square lab x sample which has (m-1) and (m-1) (s-1) degrees of freedom. Rejection of this hypothesis would mean that laboratories give different results for a given leachate sample. The hypothesis that the laboratory sample interaction variance component (σ^2_{LS}) is zero can be tested by forming the F ratio of the mean square lab x sample divided by the mean square residual which has (m-1) (s-1) and ms(n-1) degrees of freedom. Rejection of this hypothesis would mean that the relative results of the laboratories change for different leachate samples.

When only the laboratory averages are used, only the hypothesis that the between laboratory variance component is zero can be tested, as in this situation there are no degrees of freedom left to estimate the within laboratory variance component independently of the laboratory sample interaction component.

Approximate confidence intervals were computed for the estimated variance components using a method given in Searle (1971). Standard deviations were computed by taking the square root of the corresponding variance components.

When more than one method was used in the determination of a parameter, the use of a two way classification analysis of variance may not be the best way to analyze the data. In this situation a three way classification analysis of variance would be appropriate with leachate samples being crossed with laboratories and the methods used, and with laboratories being nested within methods. This was not done as the number of laboratories performing the different methods was usually very unbalanced. The use of the two way classification in these situations would still provide a useful summary of the data however.

The estimated coefficient of variations (c.v.) can be used to determine the number (m) of laboratories required for a fixed confidence interval width for the concentration level of a measured parameter in leachate. The concentration level of a parameter can be estimated by the average ($\overline{Y}$) of the laboratory averages. The standard deviation of this estimate can be calculated by σ = c.v.μ, where the c.v.^{2} = $(\sigma^2_L + \sigma^2_{LS})/m + \sigma^2_W/mn$. An approximate 95% confidence interval for the concentration is ($\overline{Y} \pm 2\sigma$). If we want to have the confidence limits range from $(1-p)\mu$ to $(1+p)\overline{\mu}$ for p between 0 and 1 then the number of laboratories required is $m=4\ (\sigma^2{}_L + \sigma^2{}_{LS})/p^2 + 4\ \sigma^2{}_W/p^2n$, where n is the number of replicates performed by each laboratory. As $\sigma^2{}_L + \sigma^2{}_{LS}$ is typically much greater than $\sigma^2{}_W$ it can be seen that more laboratories would be preferred rather than more replicates per laboratory. Also m is approximately equal to $4\ (\sigma^2{}_L + \sigma^2{}_{LS} + \sigma^2{}_W)/p^2 = 4\sigma^2{}_R/p^2 = 4\ \sigma^2{}_R/p^2$, where $\sigma^2{}_R$ is the overall reproducibility. Table 6.3 shows the number of laboratories required for several values of σ_R and p. The overall reproducibility calculated from the laboratory averages was used to compute the required number of laboratories for specified confidence limits stated for each parameter.

TABLE 6.3. NUMBER OF LABORATORIES REQUIRED FOR A 95% CONFIDENCE INTERVAL OF SPECIFIED WIDTH

				σ_R		
P in %	.05	.1	.25	.5	.75	1
5	4	16	100	400	900	1600
10	1	4	25	100	225	400
25		1	4	16	36	64
50			1	4	9	16

SECTION 7.

DETERMINATIONS

Throughout this section, the overall reproducibility (σ^2_R) is the sum of the between laboratory (σ^2_L), laboratory sample interaction (σ^2_{LS}), and within laboratory (σ^2_W) variance components; σ^2_{LPLS} is the sum of the between laboratory and laboratory sample interaction variance components. Also, when the analysis of variance is performed on the laboratory averages after omitting the data from visually outlying laboratories, the procedure is subjective and the results are not statistically defensible.

pH

Data Base

Data were received from 29 of the 49 laboratories that agreed to perform the pH analysis. The analysis was performed in triplicate by 12 laboratories for all 10 leachate samples. A single value or an average value was reported by 16 laboratories. The remaining laboratory reported an unequal number of replicates.

A summary of the analytical results for the 10 leachate samples is given in Table 7.1. The average pH level of the samples ranged from 5.59 to 7.16 pH units, with the highest value generally 1.5 units higher than the lowest value for any particular leachate sample.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.1. A regression equation was calculated to be $\sigma = .00054\ \mu + .0464$ with an R^2 value of 0%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .016 \log \mu - 1.322$ with an R^2 value of 0%. The appearance of the graphs and low R^2 values suggests that no transformation of the data is required to make the within laboratory variances at different concentration levels approximately equal.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.2. A regression equation was calculated to be $\sigma = .131\ \mu - .551$ with an R^2 value of 17%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 3.10 \log \mu - 3.08$ with an R^2 value of 24%. The appearance of the graphs and low R^2 values suggest that no transformation of the data is required to make the between laboratory variances at different concentration levels approximately equal.

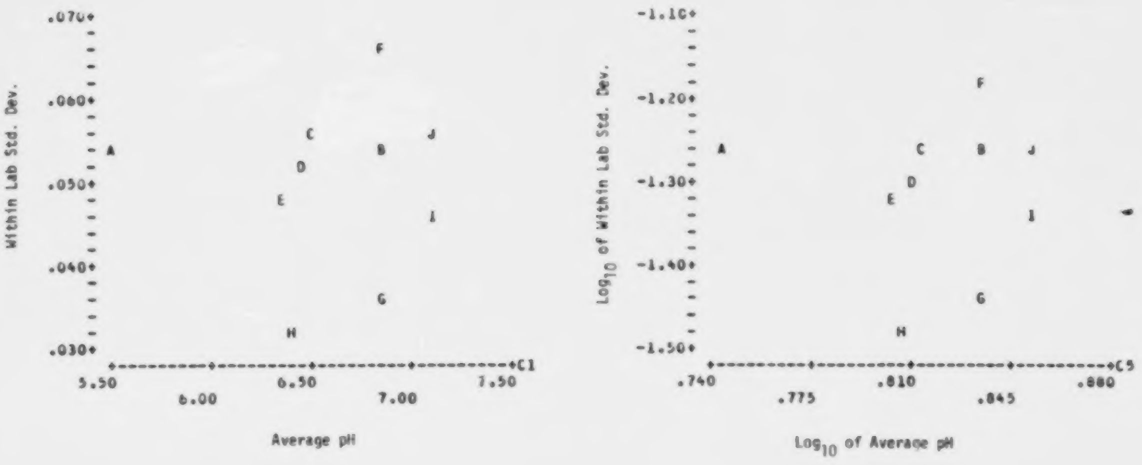

Figure 7.1. Relationship of the within laboratory standard deviation to the pH level.

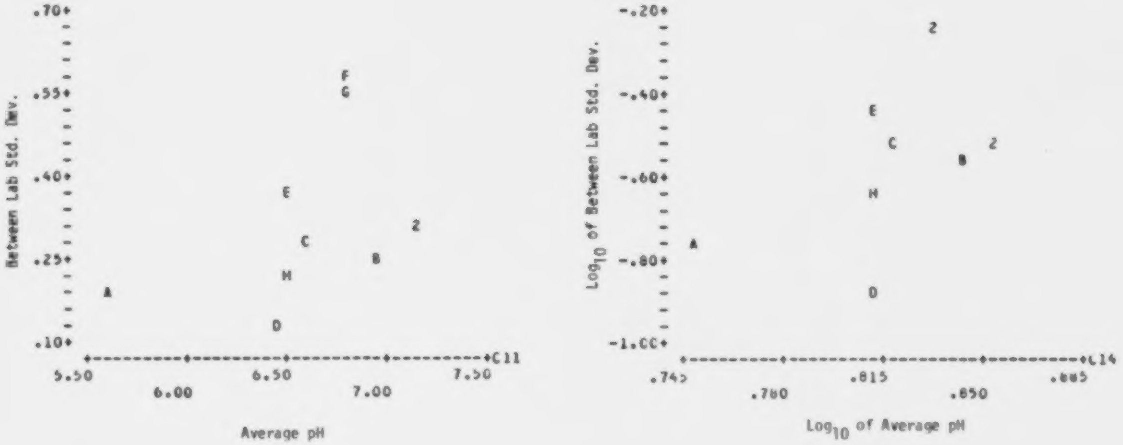

Figure 7.2. Relationship of the between laboratory standard deviation to the pH level.

The ordered laboratory averages for the pH data plotted against the quantiles from a normal distribution are shown in Figure 7.3 for the 10 leachate samples A through J. The R^2 values of a simple linear regression equation fitted to each sample are given in Table 7.2.

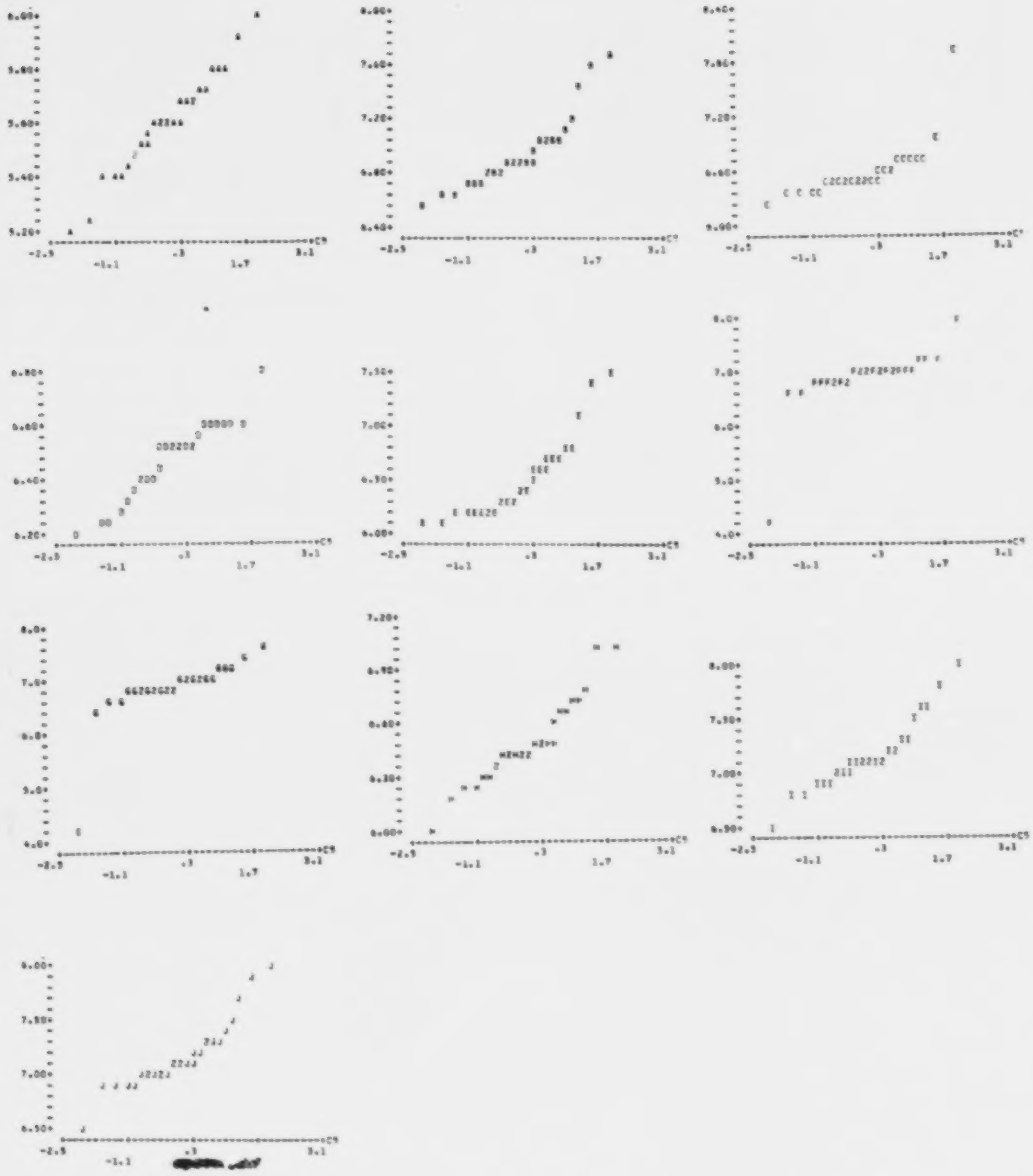

Figure 7.3. Ordered laboratory averages for pH data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

TABLE 7.1. SUMMARY OF ANALYTICAL RESULTS FOR pH DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	5.59	5.2	6.0	5.59	.054	.179
B	6.94	6.55	7.7	6.9	.054	.264
C	6.58	6.21	7.9	6.5	.056	.295
D	6.47	6.2	6.8	6.5	.051	.136
E	6.49	6.1	7.5	6.39	.048	.360
F	6.82	4.1	7.9	6.90	.066	.573
G	6.80	4.1	7.5	6.86	.037	.564
H	6.48	6.0	7.0	6.42	.033	.221
I	7.15	6.5	8.0	7.1	.046	.309
J	7.16	6.5	8.0	7.1	.055	.306

*All entries in pH units.

TABLE 7.2. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Leachate Sample										Average	Std. dev.
A	B	C	D	E	F	G	H	I	J	R^2	of R^2
98	87	62	95	84	47	50	94	92	88	80	19

It appears that the distribution of the laboratory averages for the original data is close to a normal distribution. This observation is supported by the reasonably high R^2 values for 7 of the 10 leachate samples. The low R^2 values for samples C, F, and G appear to be caused by outlying averages.

Variance Component Estimates

The data from 12 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.3. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.4.

TABLE 7.3. ANALYSIS OF VARIANCE FOR pH DATA
BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	359	80.82281		
Leachate Samples	9	70.83039		
Laboratories	11	5.63724	.51248	13.8*
Lab x Sample	99	3.70212	.03740	13.8*
Residual	240	.65307	.00272	

* $P < .005$

TABLE 7.4. VARIANCE COMPONENT ESTIMATES FOR pH DATA
BASED ON LABORATORIES REPORTING

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.0301	(.0189, .0554)	σ_R	.1735	(.1375, .2353)
σ^2_{LPLS}	.0274	(.0171, .0508)	σ_{LPLS}	.1655	(.1308, .2254)
σ^2_L	.0076	(.0076, .0509)	σ_L	.1258	(.0872, .2256)
σ^2_{LS}	.0116	(.0087, .0160)	σ_{LS}	.1075	(.0935, .1265)
σ^2_W	.0027	(.0023, .0033)	σ_W	.0522	(.0479, .0573)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.5. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.6.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .14$, $\sigma_L = .10$, and $\sigma = .10$. These values are smaller than the corresponding estimates given in Table 7.6, which indicates that greater precision may be attainable.

TABLE 7.5. ANALYSIS OF VARIANCE FOR pH DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	289	88.1221		
Leachate Samples	9	53.9446		
Laboratories	28	9.2401	.3300	3.33*
Residual	252	24.9373	.0990	

* P < .005

TABLE 7.6. VARIANCE COMPONENT ESTIMATES FOR pH DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.1221	(.1018, .1492)	σ_R	.3494	(.3191, .3862)
σ^2_L	.0129	(.0128, .0585)	σ_L	.1520	(.1108, .2418)
σ^2*	.0990	(.0838, .1188)	σ**	.3146	(.2894, .3447)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

ORP Data Base

Data were received from 11 of the 18 laboratories that agreed to perform the ORP analysis. The analysis was performed in triplicate by 6 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 3 laboratories. The remaining laboratory reported an unequal number of replicates.

A summary of the analytical results for the 10 leachate samples is given in Table 7.7. The average ORP level of the samples ranged from -201 to 60.3 mv, with the highest value generally 400 mv larger than the lowest value for any particular leachate sample.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average is shown in Figure 7.4. A regression equation was calculated to be $\sigma = .0458\ \mu + 28.4$ with an R^2 value of 4%. The appearance of this graph and low R^2 value suggest that no transformation of the data is required to make the within laboratory variances at different concentration levels approximately equal for the transformed data.

TABLE 7.7. SUMMARY OF ANALYTICAL RESULTS FOR ORP DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	-103	-535	146	-12.1	62.0	222
B	-158	-348	- 92	-142	31.1	69.3
C	-147	-370	- 59	-142	17.6	84.9
D	-140	-378	- 58.3	-142	14.6	87.0
E	-138	-343	83.6	-148	12.5	105.
F	-196	-427	-125	-183	8.33	81.2
G	-201	-432	- 98	-190	10.7	84.4
H	-159	-424	- 65	-152	11.6	104
I	- 61.6	-406	139	- 65	44.7	160
J	60.3	-347	173	117.5	7.5	155

*All entries in mv.

The between laboratory standard deviation plotted against the average is shown in Figure 7.5. A regression equation was calculated to be $\sigma = .386\ \mu + 163$ with an R^2 value of 37%. The appearance of this graph and low R^2 value suggests that no transformation of the data is required to make the between laboratory variances at different concentration levels approximately equal for the transformed data.

Although no transformation was indicated to stabilize the within and between laboratory variances, the choice of a transformation is somewhat uncertain as, with the exception of leachate sample J, the variability does appear to increase with increasing ORP levels. Further, if a transformation like the square root or logarithm was indicated, the presence of both negative and positive values in the reported results would become a problem.

The ordered laboratory averages for the ORP data plotted against the quantiles from a normal distribution are shown in Figure 7.6 for the 10 leachate samples A through J. The R^2 values of a simple linear regression equation fitted to each sample are given in Table 7.8.

It appears that the distribution of the laboratory averages for the original data is close to a normal distribution. This observation is supported by the somewhat high R^2 values for the leachate samples. A single outlying avarage is present in most of the leachate samples, however, which will affect the R^2 values.

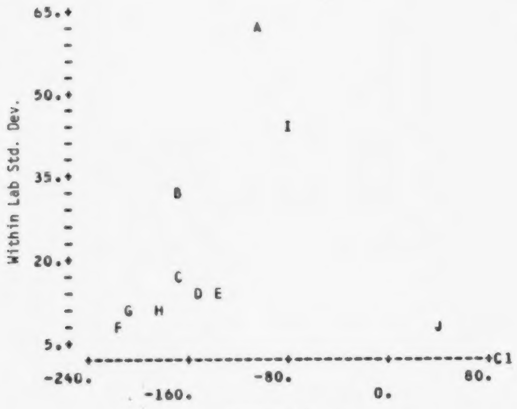

Figure 7.4. Relationship of the within laboratory standard deviation to the ORP level.

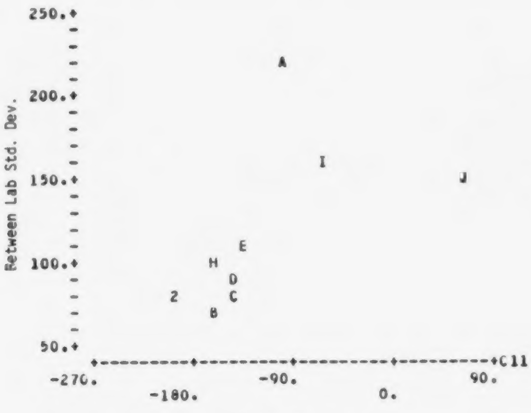

Figure 7.5. Relationship of the between laboratory standard deviation to the ORP level.

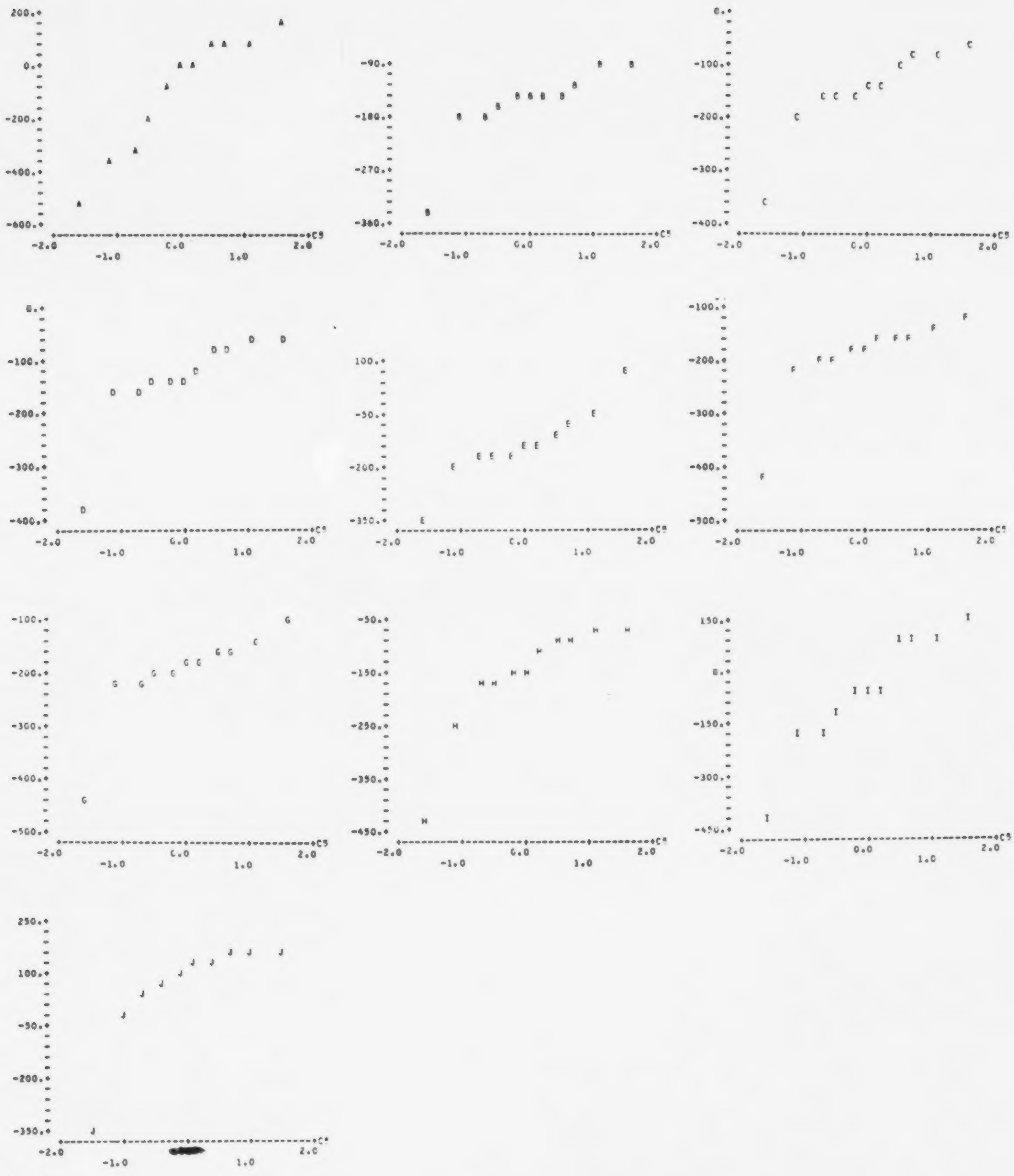

Figure 7.6. Ordered laboratory averages for ORP data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

TABLE 7.8. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Leachate Sample										Average R^2	Std. dev. of R^2
A	B	C	D	E	F	G	H	I	J		
91	71	78	70	92	65	72	79	92	68	78	10

The data from 6 labotatories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.9. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.10.

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.11. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.12.

TABLE 7.9. ANALYSIS OF VARIANCE FOR ORP DATA
BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	179	4253408.	--	--
Leachate Samples	9	1035683.	--	--
Laboratories	5	2447412.	489482.	33.3*
Lab x Sample	45	661989.	14711.	16.3*
Residual	120	108323.	903	--

* $P < .005$

TABLE 7.10. VARIANCE COMPONENT ESTIMATES FOR ORP DATA BASED ON LABORATORIES REPORTING THREE REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	21331	(9906, 74615)	σ_R	146.1	(99.5, 273.2)
σ^2_{LPLS}	20428	(9231, 76884)	σ_{LPLS}	142.9	(96.1, 277.3)
σ^2_L	15826	(6030, 103193)	σ_L	125.8	(77.7, 321.2)
σ^2_{LS}	4603	(3907, 7559)	σ_{LS}	67.8	(55.6, 86.9)
σ^2_W	903	(712, 1183)	σ_W	30.1	(26.7, 34.4)

TABLE 7.11. ANALYSIS OF VARIANCE FOR ORP DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	109	2096486.	--	--
Leachate Samples	9	580543.	--	--
Laboratories	10	933460.	93346.	14.4*
Residual	90	582483.	6472.	--

* P < .005

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = 75$, $\sigma_L = 39$, and $\sigma = 64$. These values are smaller than the corresponding estimates given in Table 7.12, which indicates that greater precision may be attainable.

TABLE 7.12. VARIANCE COMPONENT ESTIMATES FOR ORP DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	15159	(9343, 28779)	σ_R	123.1	(96.7, 169.6)
σ^2_L	8687	(4060, 29877)	σ_L	93.2	(63.7, 172.8)
σ^2*	6472	(4930, 8874)	σ**	80.4	(70.2, 94.2)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Turbidity Data Base

Data were received from 22 of the 39 laboratories that agreed to perform the turbidity analysis. The analysis was performed in triplicate by 7 laboratories for all 10 leachate samples. A single value or an average value was reported by 10 laboratories. The remaining 5 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value) for this parameter. One 0 turbidity reading was reported for leachate sample E.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.7. A regression equation was calculated to be $\sigma = .98 \log \mu - 1.01$ with an R^2 value of 84%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.64, 1.32), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

A summary of the analytical results for the 10 leachate samples is given in Table 7.13. The average turbidity level of the samples ranged from 15.4 to 1085 turbidity units, with the highest value generally 1000 times larger than the lowest value for any particular leachate sample.

TABLE 7.13 SUMMARY OF ANALYTICAL RESULTS FOR TURBIDITY DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	205	0.7	1690	65	12.7	387
B	808	0.03	4687	340	60.7	1132
C	519	0.33	2000	248	34.0	638
D	1085	10	6233	245	235	1580
E	349	0	1683	110	59.8	522
F	560	5.8	3233	340	137	727
G	499	3.1	1660	160	136	613
H	469	15	2100	241	80.3	549
I	261	15	943	260	86.7	207
J	15.4	5.3	110	11	1.1	22.3

*All entries in turbidity units.

The ordered laboratory averages for the turbidity data plotted against the quantiles from a normal distribution are shown in Figure 7.9 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.10. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.14

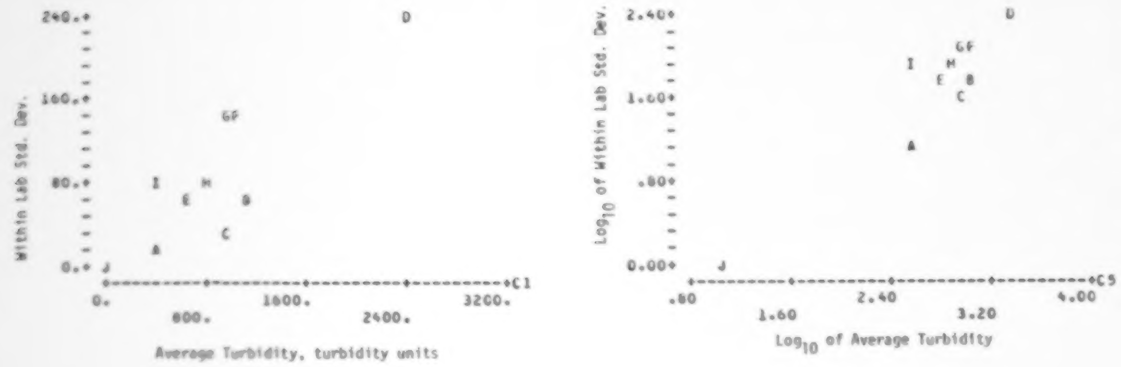

Figure 7.7. Relationship of the within laboratory standard deviation to the turbidity level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.8. A regression equation was calculated to be $\sigma = 1.44\ \mu - 47$ with an R^2 value of 97%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .979 \log \mu + .173$ with an R^2 value of 97%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.83, 1.13), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, .005 was added to all zero (0) values. These transformed data were used in the statistical analysis of this parameter.

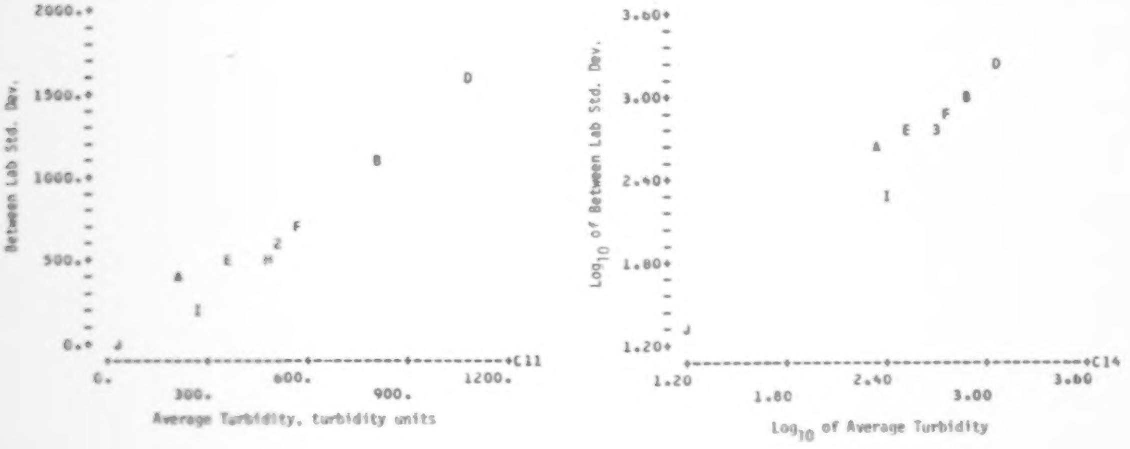

Figure 7.8 Relationship of the between laboratory standard deviation to the turbidity level.

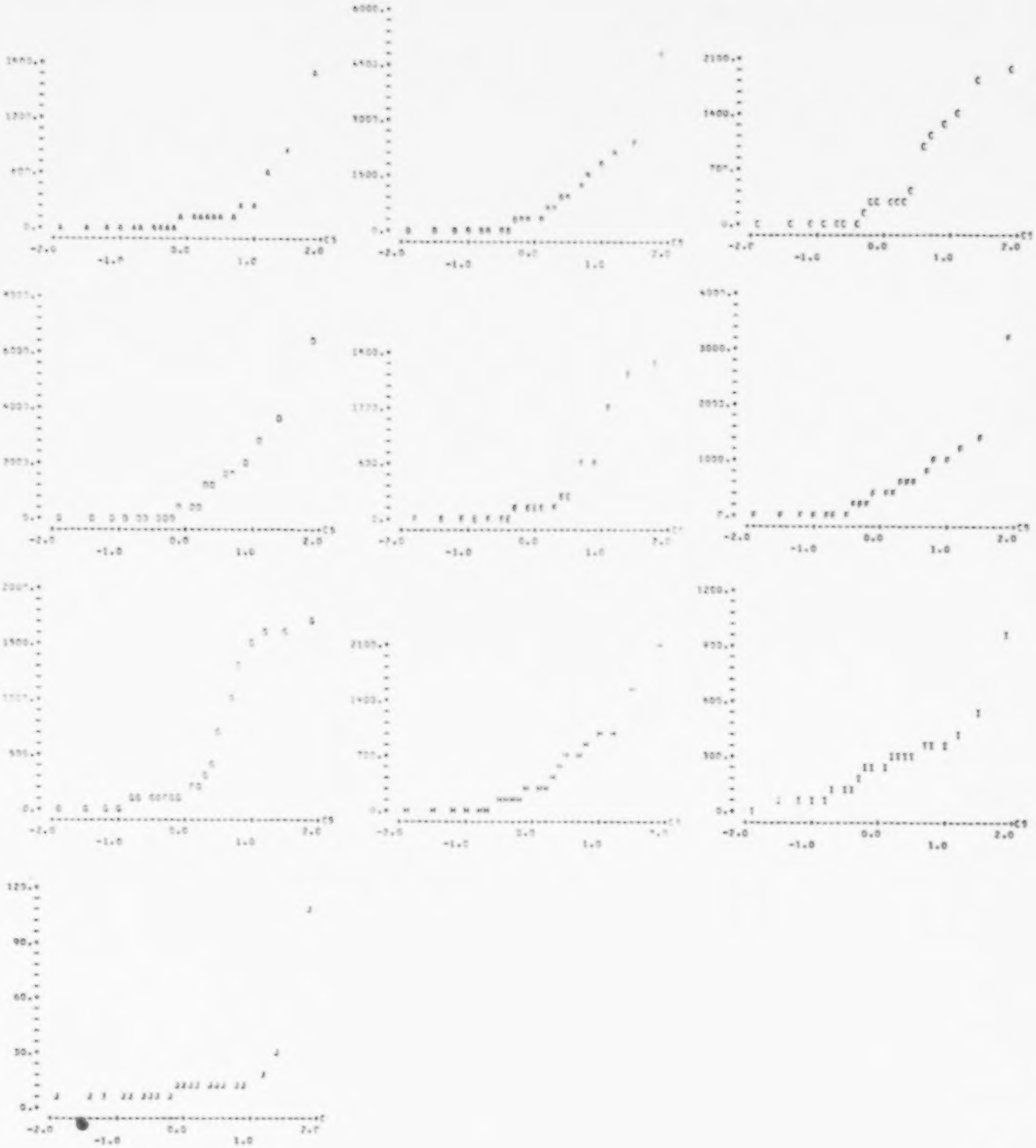

Figure 7.9. Ordered laboratory averages for turbidity data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

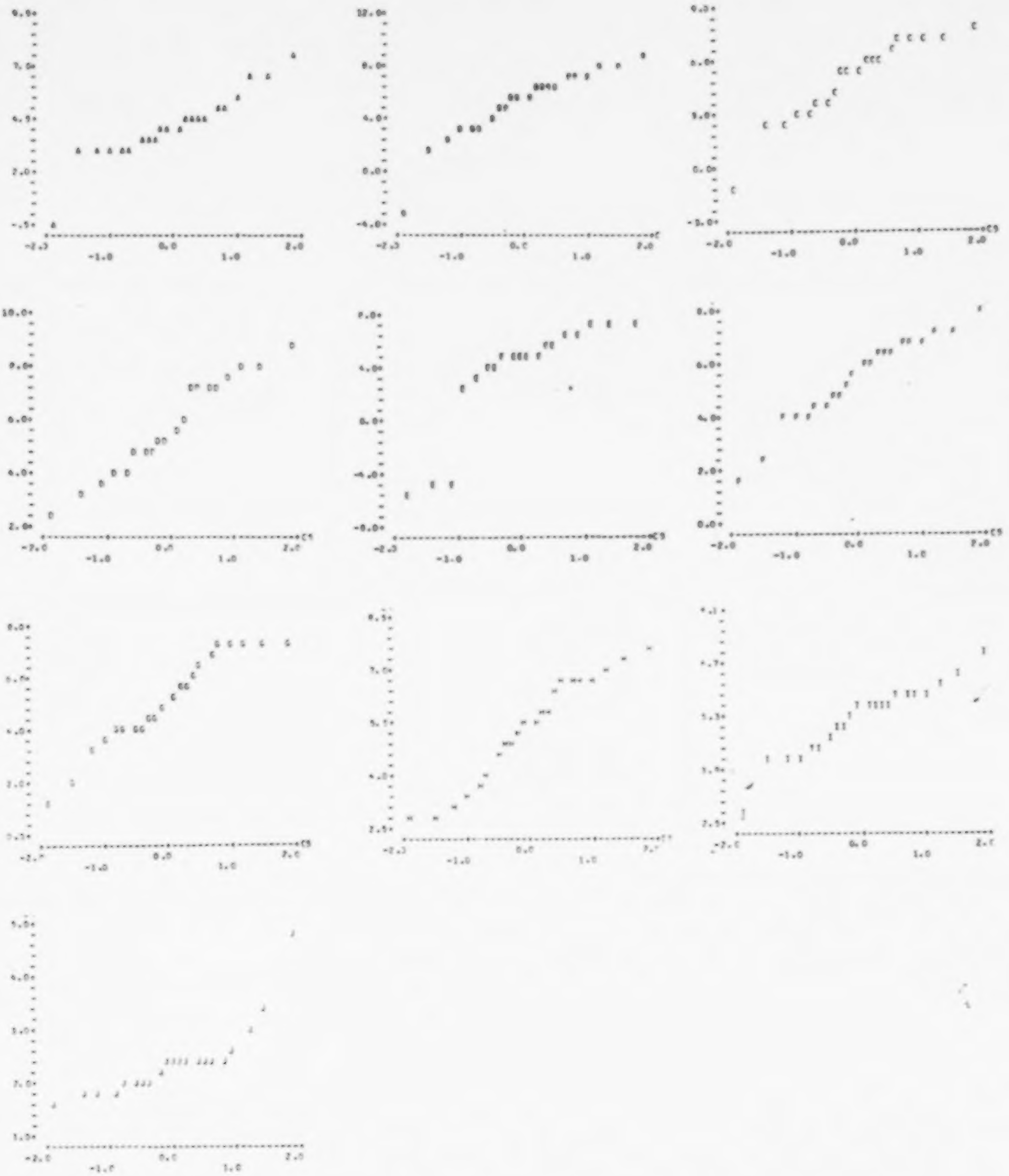

Figure 7.10. Ordered laboratory averages for $\log_e$ transformed turbidity data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

TABLE 7.14 R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average R^2	Std. dev. of R^2
	A	B	C	D	E	F	G	H	I	J		
Original	51	72	80	70	69	70	76	80	84	37	69	14
Transformed	92	86	91	97	77	96	95	96	93	75	90	8

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for all 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in some of the leachate samples, however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed turbidity data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 7 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.15. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.16.

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.17. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.18.

TABLE 7.15. ANALYSIS OF VARIANCE FOR LOG$_e$ TURBIDITY DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	209	701.2123		
Leachate Samples	9	316.8314		
Laboratories	6	190.7543	31.7924	8.95*
Lab x Sample	54	191.8125	3.5521	273*
Residual	140	1.8142	.0130	

* P < .005

TABLE 7.16. VARIANCE COMPONENT ESTIMATES FOR LOG$_e$ TURBIDITY DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	2.1340	(1.2744, 4.2878)	σ_R	1.4608	(1.1289, 2.0707)
σ^2_{LPLS}	2.1210	(1.2632, 4.2827)	σ_{LPLS}	1.4564	(1.1239, 2.0695)
σ^2_L	.9413	(.3593, 6.0959)	σ_L	.9702	(.5994, 2.4690)
σ^2_{LS}	1.1797	(.8351, 1.7936)	σ_{LS}	1.0861	(.9138, 1.3392)
σ^2_W	.0130	(.0104, .0167)	σ_W	.1140	(.1021, .1291)

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = 1.3$, $\sigma_L = .88$, and $\sigma = .95$. These values are smaller than the corresponding estimates given in Table 7.18, which indicates that greater precision may be attainable.

TABLE 7.17. ANALYSIS OF VARIANCE FOR LOG$_e$ TURBIDITY DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	219	1060.48	--	--
Leachate Samples	9	210.09	--	--
Laboratories	21	490.92	23.38	12.3*
Residual	189	359.47	1.90	--

* $P < .005$

TABLE 7.18. VARIANCE COMPONENT ESTIMATES FOR LOG$_E$ TURBIDITY DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	4.0480	(2.9114, 6.0136)	σ_R	2.0120	(1.7063, 2.4523)
σ^2_L	2.1480	(1.2212, 4.7363)	σ_L	1.4656	(1.1051, 2.1763)
σ^2*	1.9000	(1.5684, 2.3499)	σ**	1.3784	(1.2523, 1.5329)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Conductivity Data Base

Data were received from 29 of the 45 laboratories that agreed to perform the conductivity analysis. The analysis was performed in triplicate by 12 laboratories for all 10 leachate samples. A single value or an average value was reported by 15 laboratories. The remaining 2 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value), and no 0 µmhos/cm conductivity levels were reported.

A summary of the analytical results for the 10 leachate samples is given in Table 7.19. The average conductivity level of the samples ranged from 1793 to 56,407 μmhos/cm, with the highest value generally 10 times larger than the lowest value for any particular leachate sample.

TABLE 7.19. SUMMARY OF ANALYTICAL RESULTS FOR CONDUCTIVITY DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	56407	7000	95080	56367	1588	17215
B	5979	3667	25400	5500	178	3804
C	15014	12000	18850	14550	324	1868
D	8549	830	11383	9200	164	1932
E	5003	2733	39500	3838	75.3	6776
F	3185	1733	23200	2591	47.6	3863
G	4333	2200	33700	3323	76.2	5675
H	1793	953	10000	1517	48.7	1596
I	6307	1200	42900	5200	78	7096
J	1862	650	10000	925	19.1	2773

*All entries in μmhos/cm.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.11. A regression equation was calculated to be $\sigma = .029\ \mu - 35.7$ with an R^2 value of 99%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.03 \log \mu - 1.75$ with an R^2 value of 97%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.88, 1.18), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within laboratory variance. Although the square root transformation was indicated to stabilize the between laboratory variance, the appearance of the graphs and low R^2 value makes the choice of a transformation uncertain. The logarithmic transformed data were used in the statistical analysis of this parameter.

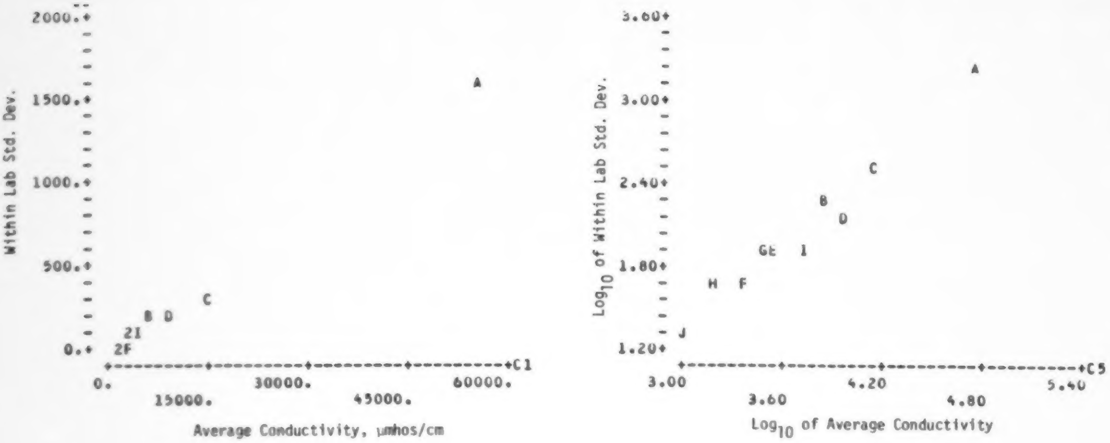

Figure 7.11 Relationship of the within laboratory standard deviation to the conductivity level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.12. A regression equation was calculated to be $\sigma = .242\ \mu + 2630$ with an R^2 value of 74%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .395 \log \mu + 2.11$ with an R^2 value of 30%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (-.10, .89), which suggests that a square root transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

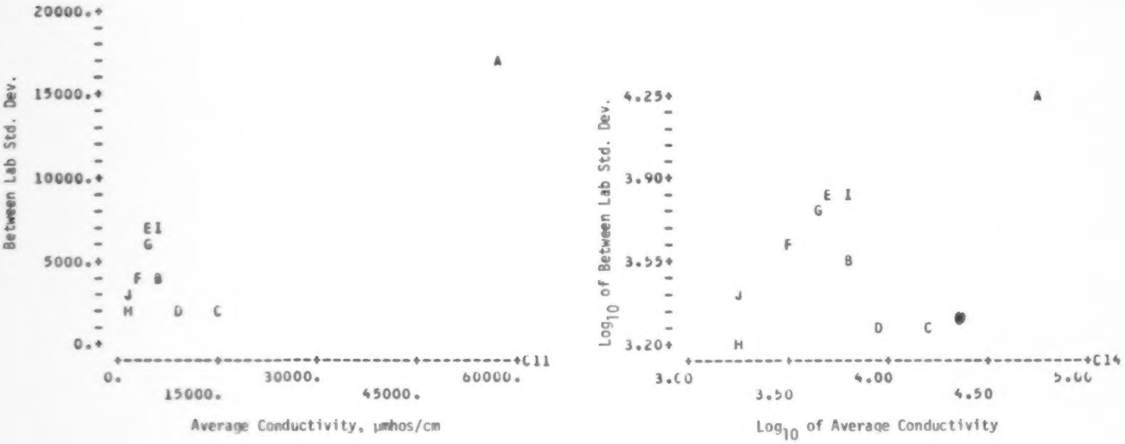

Figure 7.12. Relationship of the between laboratory standard deviation to the conductivity level.

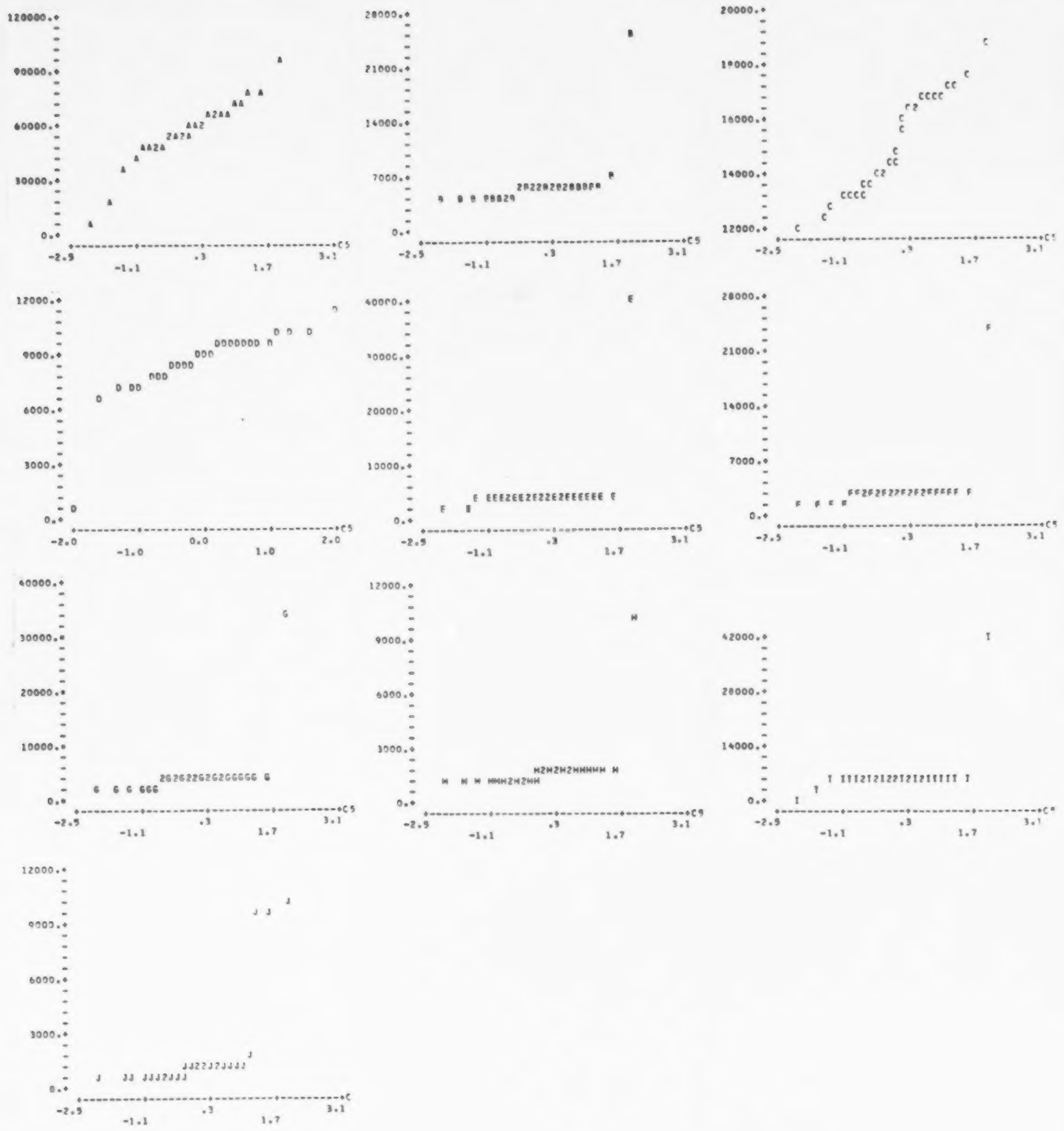

Figure 7.13. Ordered laboratory averages for conductivity data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J,respectively.

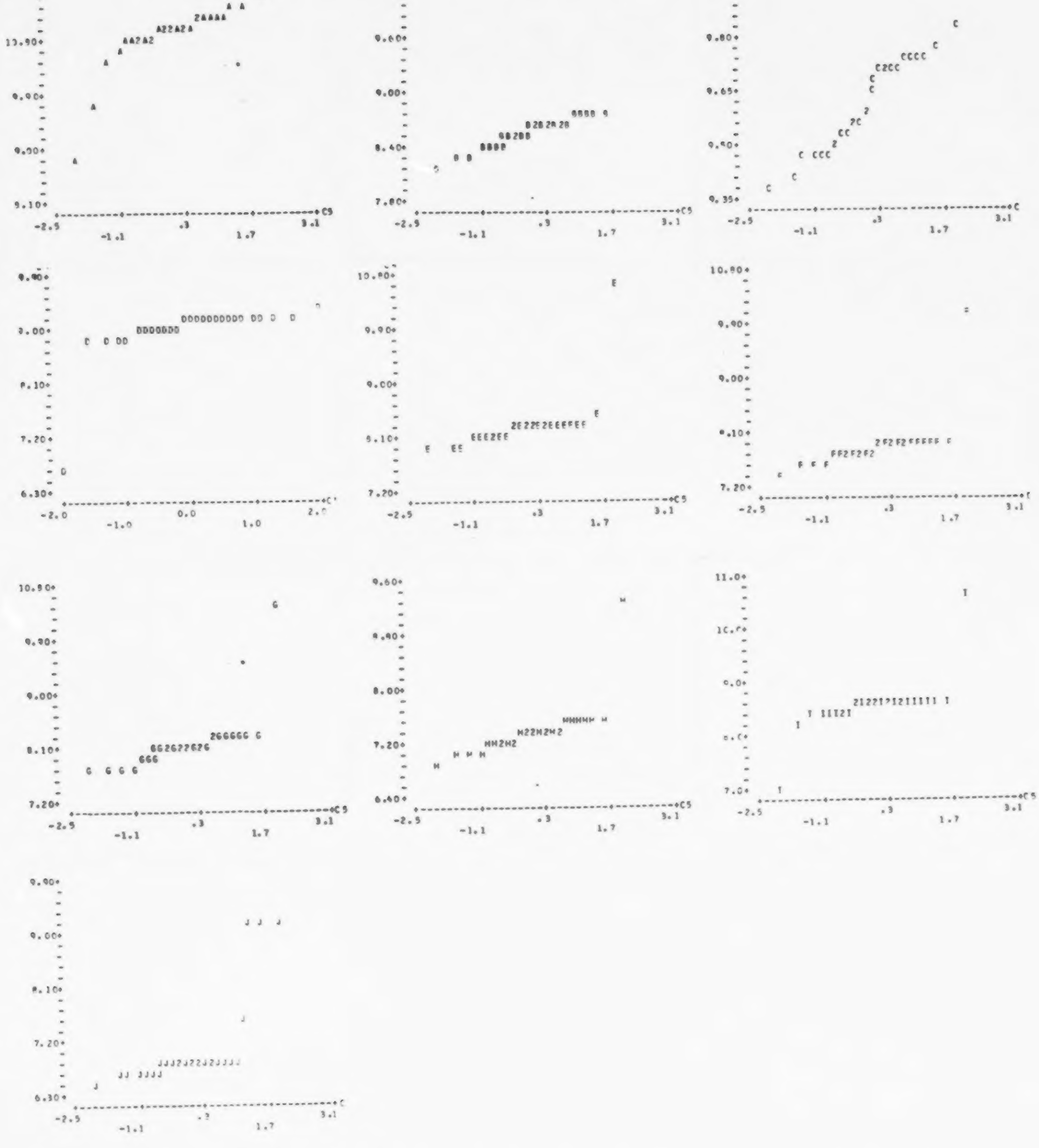

Figure 7.14 . Ordered laboratory averages for $\log_e$ transformed conductivity data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

The ordered laboratory averages for the conductivity data plotted against the quantiles from a normal distribution are shown in Figure 7.13 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.14. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.2.

TABLE 7.20 R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average	Std. dev.
	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	92	32	95	74	22	23	24	28	25	40	46	30
Transformed	66	57	95	42	40	44	51	55	51	51	55	16

For the original data it appears that the distribution of the laboratory averages has a lighter lower tail and a heavier upper tail than the lower and upper tails of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data, (i.e. closer to a straight line). This observation is supported by the R^2 values for 7 of the 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples however, which appear to be responsible for the low R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are the $\log_e$ transformed conductivity data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 12 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.21. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.22.

TABLE 7.21. ANALYSIS OF VARIANCE FOR LOG_e CONDUCTIVITY DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	359	464.57032	--	--
Leachate Samples	9	449.28702	--	--
Laboratories	11	6.09480	.55407	6.07*
Lab x Sample	99	9.03079	.09122	138 *
Residual	240	.15770	.00066	--

* P < .005

TABLE 7.22 VARIANCE COMPONENT ESTIMATES FOR LOG_e CONDUCTIVITY DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.0463	(.0328, .0703)	σ_R	.2151	(.1810, .2651)
σ^2_{LPLS}	.0456	(.0323, .0693)	σ_{LPLS}	.2136	(.1798, .2632)
σ^2_L	.0154	(.0069, .0589)	σ_L	.1242	(.0833, .2427)
σ^2_{LS}	.0302	(.0232, .0408)	σ_{LS}	.1737	(.1524, .2021)
σ^2_W	.0007	(.0006, .0008)	σ_W	.0257	(.0236, .0282)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.23. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.24.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .14$, $\sigma_L = .11$, and $\sigma = .097$. These values are considerably smaller than the corresponding estimates given in Table 7.24, which indicates that greater precision may be attainable.

TABLE 7.23. ANALYSIS OF VARIANCE FOR LOG$_e$ CONDUCTIVITIY DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	289	377.772	--	--
Leachate Samples	9	317.352	--	--
Laboratories	28	18.734	.669	4.06*
Residual	252	41.686	.165	--

* $P < .005$

TABLE 7.24. VARIANCE COMPONENT ESTIMATES FOR LOG$_e$ CONDUCTIVITY DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.2154	(.1777, .2666)	σ_R	.4641	(.4215, .5164)
σ^2_L	.0504	(.0278, .1176)	σ_L	.2245	(.1669, .3429)
σ^2*	.1650	(.1396, .1981)	σ**	.4062	(.3736, .4451)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Free Volatile Fatty Acids Data Base

Data were received from 12 of the 20 laboratories that agreed to perform the free volatile fatty acids analysis. The analysis was performed in triplicate by 7 laboratories for all 10 leachate samples. A single value or an average value was reported by 2 laboratories. The remaining 3 laboratories reported an unequal number of replicates.

Seven values reaging from 50 to 100 mg/ℓ were reported as detection limits by 2 laboratories (i.e., < value). A complete listing of these values is given in Table A-1 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Eighteen 0 mg/ℓ concentration levels were reported for leachate samples G, I, and J with frequency 3, 6 and 9, respectively.

A summary of the analytical results for the 10 leachate samples is given in Table 7.25 . The average free volatile fatty acids concentration of the samples ranged from 131 to 11,091 mg/ℓ, with the highest value generally 10 times larger than the lowest value for any particular leachate sample.

TABLE 7.25. SUMMARY OF ANALYTICAL RESULTS FOR FREE VOLATILE FATTY ACIDS DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	11091	4163	14416	11472	354	3330
B	1193	20.7	4780	858	106	1384
C	7303	3905	10880	7303	205	1701
D	4896	2012	6817	4856	236	1245
E	1514	462	2960	1559	143	658
F	497	115	1260	367	111	365
G	355	0	1860	155	67.1	519
H	1113	212	4210	681	140	1146
I	146	0	428	87.5	38.1	142
J	131	0	1088	32.8	22.9	306

*All entries in mg/ℓ .

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.15. A regression equation was calculated to be $\sigma = .025\ \mu + 69.8$ with an R^2 value of 87%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .525 \log \mu + .426$ with an R^2 value of 90%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.38, .67), which suggests that a square root transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

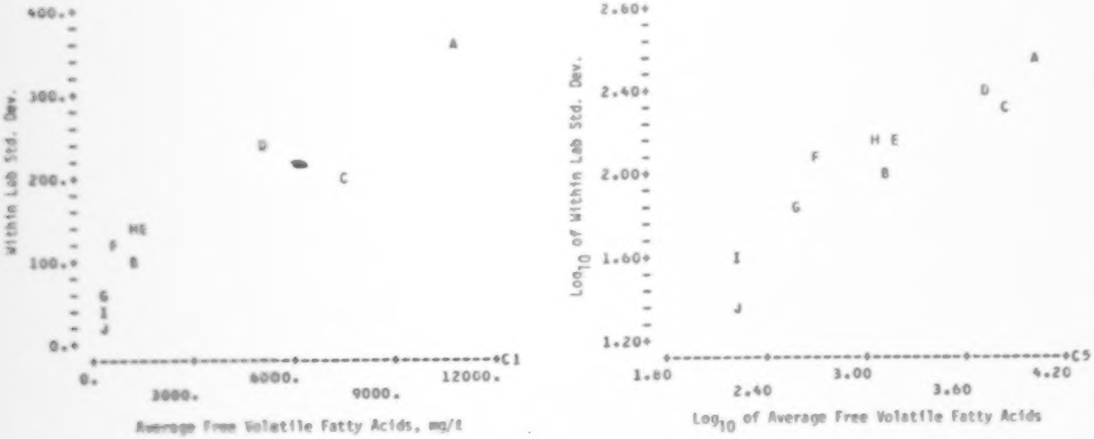

Figure 7.15. Relationship of the within laboratory standard deviation to the free volatile fatty acids concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.16. A regression equation was calculated to be $\sigma = .233\ \mu + 422$ with an R^2 value of 85%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .552 \log \mu + 1.20$ with an R^2 value of 84%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.35, .75), which suggests that a square root transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

Although the square root transformation was indicated to stabilize the within and between laboratory variances, the natural logarithms of the reported concentration levels were taken and were used in the statistical analysis of this parameter. This was done as free volatile fatty acids was the only parameter where the square root transformation was indicated to stabilize both variances, and the logarithmic transformation was found to be adequate in analyzing these data for the first time. Before applying the transformation, 6.5 was added to all zero values.

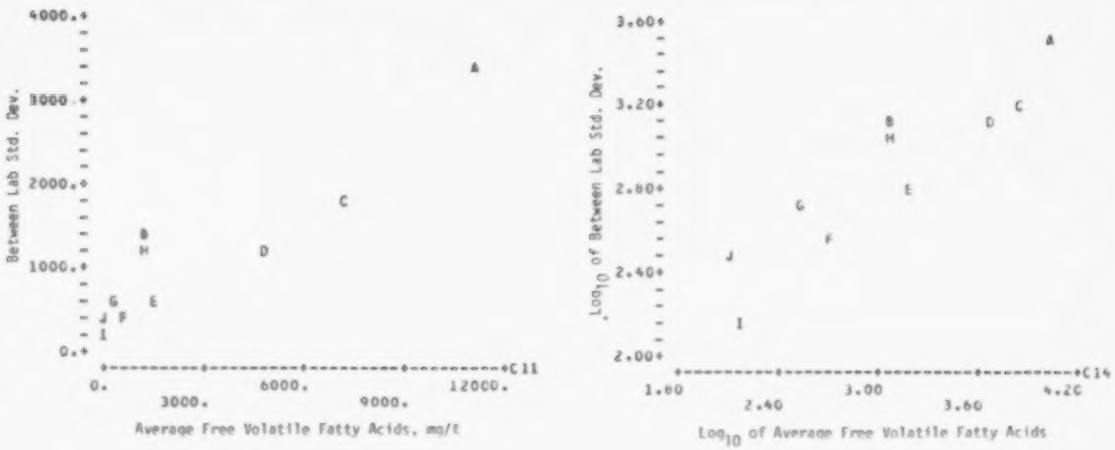

Figure 7.16 Relationship of the between laboratory standard deviation to the free volatile fatty acids concentration level.

The ordered laboratory averages for the free volatile fatty acids data plotted against the quantiles from a normal distribution are shown in Figure 7.17 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.18. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.26

TABLE 7.26 R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample A	B	C	D	E	F	G	H	I	J	Average R^2	Std. dev. of R^2
Original	84	74	94	82	94	78	63	68	86	44	77	15
Transformed	74	88	90	77	92	93	96	94	89	90	88	7

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e ,closer to a straight line). This observation is supported by the higher R^2 values for 6 of the 10 leachate samples, the greater average R^2 , and smaller standard deviation of the R^2 values for the log transformed data than were obtained for the original data. Outlying averages are present in some of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

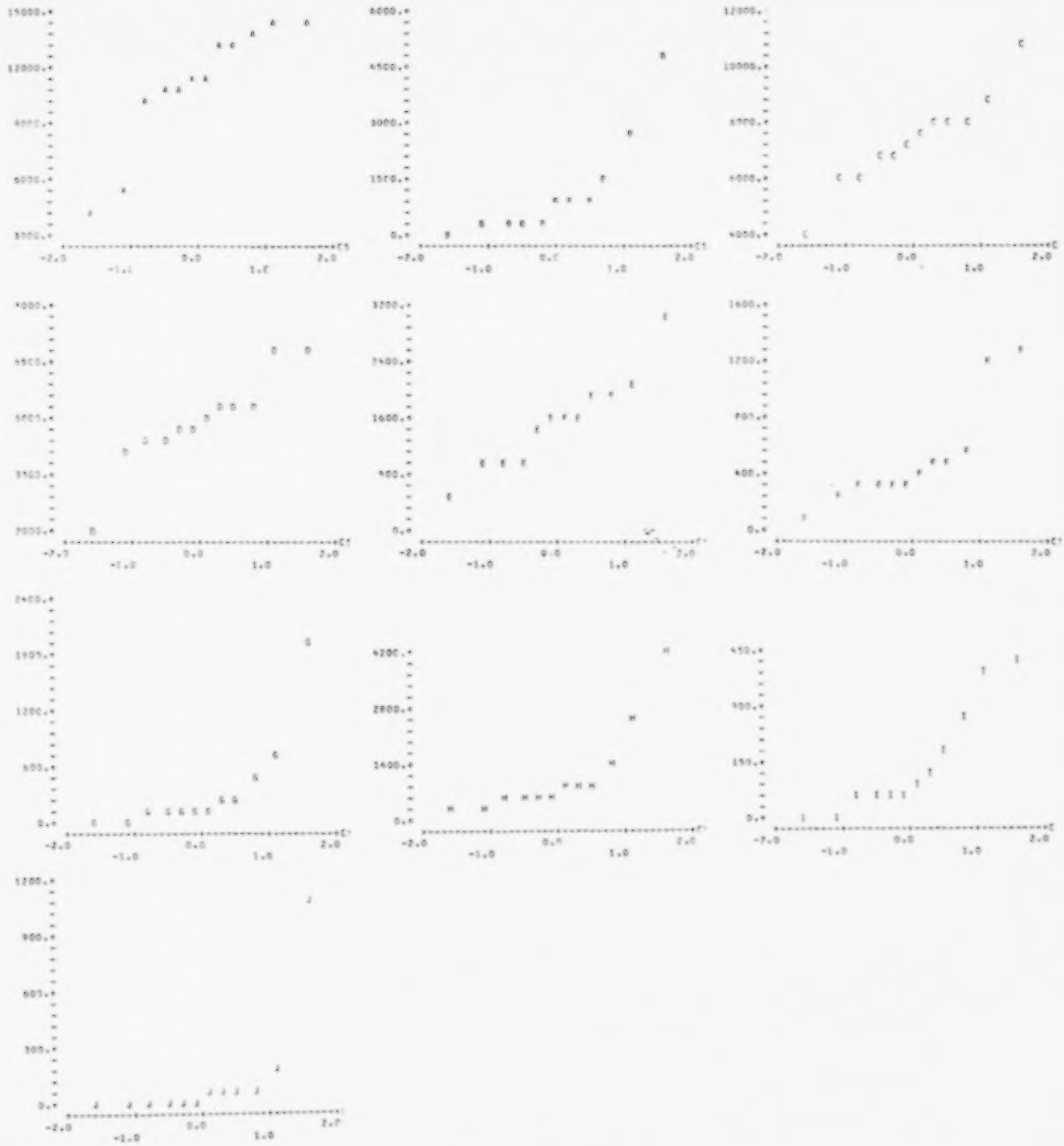

Figure 7.17 Ordered laboratory averages for free volatile fatty acids data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

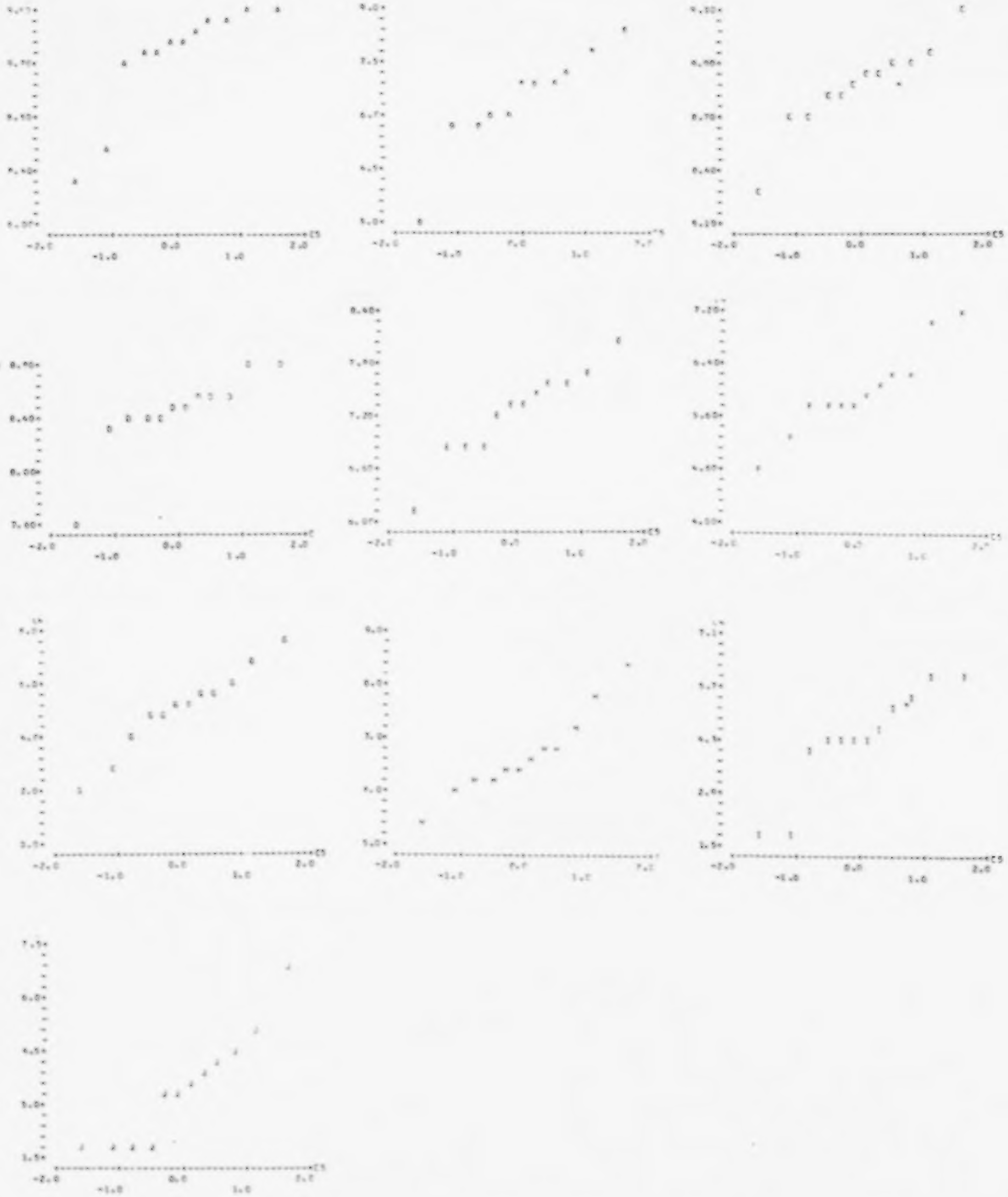

Figure 7.18. Ordered laboratory averages for $\log_e$ transformed free volatile fatty acids data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_{e}$ transformed free volatile fatty acids data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 7 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.27. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.28.

TABLE 7.27. ANALYSIS OF VARIANCE FOR LOG_e FREE VOLATILE FATTY ACIDS DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	209	899.2841	--	--
Leachate Samples	9	655.672	--	--
Laboratories	6	120.6741	20.1123	9.07*
Lab x Sample	54	119.759	2.2178	97.7 *
Residual	140	3.1791	.0227	--

* $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.29. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.30.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .66$, $\sigma_L = .34$, and $\sigma = .57$. These values are smaller than the corresponding estimates given in Table 7.30, which indicates that greater precision may be attainable.

TABLE 7.28. VARIANCE COMPONENT ESTIMATES FOR LOG_e FREE VOLATILE FATTY ACIDS DATA BASED ON LABORATORIES REPORTING THREE REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.3509	(.8073, 2.7107)	σ_R	1.1623	(.8985, 1.6464)
σ^2_{LPLS}	1.3282	(.7877, 2.7016)	σ_{LPLS}	1.1525	(.8875, 1.6436)
σ^2_L	.5965	(.2280, 3.8455)	σ_L	.7723	(.4774, 1.9610)
σ^2_{LS}	.7317	(.5169, 1.1159)	σ_{LS}	.8554	(.7189, 1.0564)
σ^2_W	.0227	(.0182, .0291)	σ_W	.1507	(.1349, .1706)

TABLE 7.29. ANALYSIS OF VARIANCE FOR LOG_e FREE VOLATILE FATTY ACIDS DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Squares	F
Total	119	512.708	--	--
Leachate Samples	9	400.851	--	--
Laboratories	1	50.150	4.559	7.32*
Residual	99	61.707	.623	--

* $P < .005$

COD Data Base

Data were received from 25 of the 46 laboratories that agreed to perform the COD analysis. The analysis was performed in triplicate by 10 laboratories for all 10 leachate samples. A single value or an average was reported by 7 laboratories. The remaining 8 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value) for this parameter, and no 0 mg/ℓ concentration levels were reported.

TABLE 7.30 . VARIANCE COMPONENT ESTIMATES FOR LOG$_e$ FREE FATTY VOLATILE ACIDS DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.0166	(.7040, 1.5970)	σ_R	1.0083	(.8391, 1.2637)
σ^2_L	.3936	(.1808, 1.4178)	σ_L	.6274	(.4252, 1.1907)
σ^2*	.6230	(.4803, .8408)	σ**	.7893	(.6930, .9170)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

A summary of the analytical results for the ten leachate samples is given in Table 12.1 . The average COD concentration of the samples ranged from 98.4 to 27,284 mg/ℓ, with the highest value generally 5 times larger than the lowest value for any particular leachate sample.

TABLE 7.31 SUMMARY OF ANALYTICAL RESULTS FOR COD DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	27284	14933	40121	28700	990	5669
B	2168	816	8737	1888	310	1592
C	16084	5900	24876	16208	531	3259
D	10719	5900	17283	10990	423	2318
E	3408	1400	5488	3833	146	1154
F	2047	1074	4314	1962	259	705
G	945	380	1792	895	53.1	365
H	1298	580	1860	1329	143	271
I	423	295	940	394.	22.3	123
J	98.4	57.3	193	84.5	7.76	33.2

*All entries in mg/ℓ.

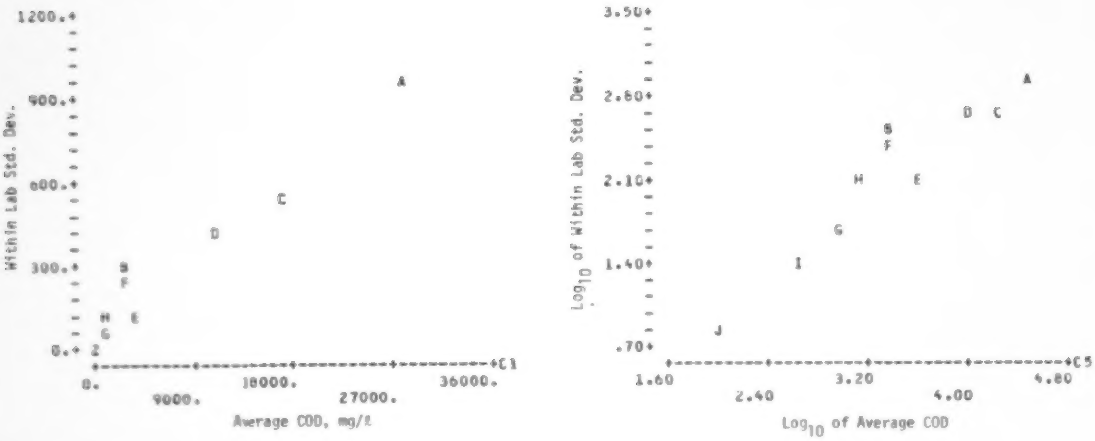

Figure 7.19. Relationship of the within laboratory standard deviation to the COD concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.20. A regression equation was calculated to be $\sigma = .195\ \mu + 290$ with an R^2 value of 96%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .904 \log \mu - .198$ with an R^2 value of 95%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.73, 1.08), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

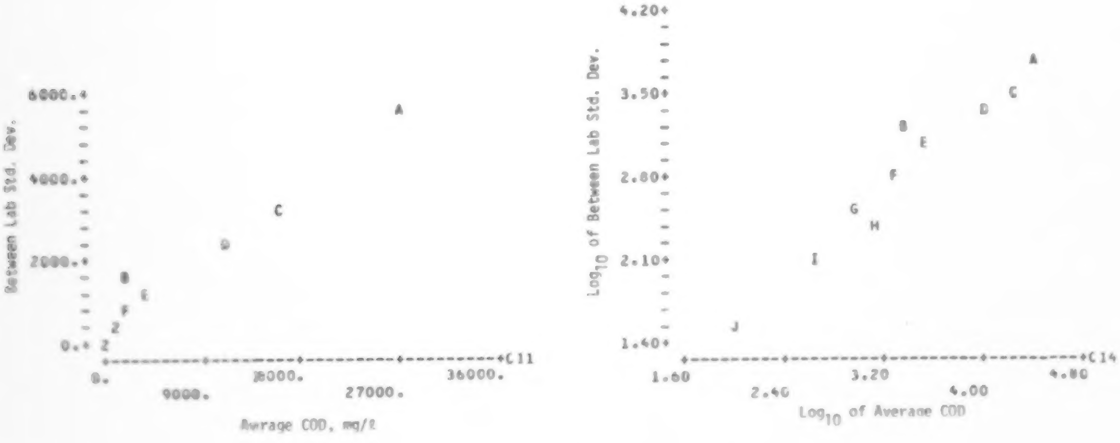

Figure 7.20. Relationship of the between laboratory standard deviation to the COD concentration level.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.19. A regression equation was calculated to be $\sigma = .0318\ \mu + 77.1$ with an R^2 value of 93%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .833 \log \mu - .656$ with an R^2 value of 92%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.63, 1.04), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The ordered laboratory averages for the COD data plotted against the quantiles from a normal distribution are shown in Figure 7.21 for the ten leachate samples A through J. The corresponding plots for the log transformed data are shown in Figure 7.22 . The R^2 values of a simple linear regression equation fitted to each sample for both the original and log transformed data are given in Table 7.32.

TABLE 7.32 . R^2 VALUES

	Leachate Sample										Average	Std. dev.
Data	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	92	63	83	84	92	80	96	89	62	81	82	12
Transformed	87	92	70	82	86	90	99	77	78	91	85	9

The distribution of the laboratory averages for the log transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for 5 of the 10 leachate samples, the slightly greater average R^2 , and smaller standard deviation of the R^2 values for the log transformed data than were obtained for the original data. Several outlying averages are present in some of the leachate samples, however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed COD data, and this the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

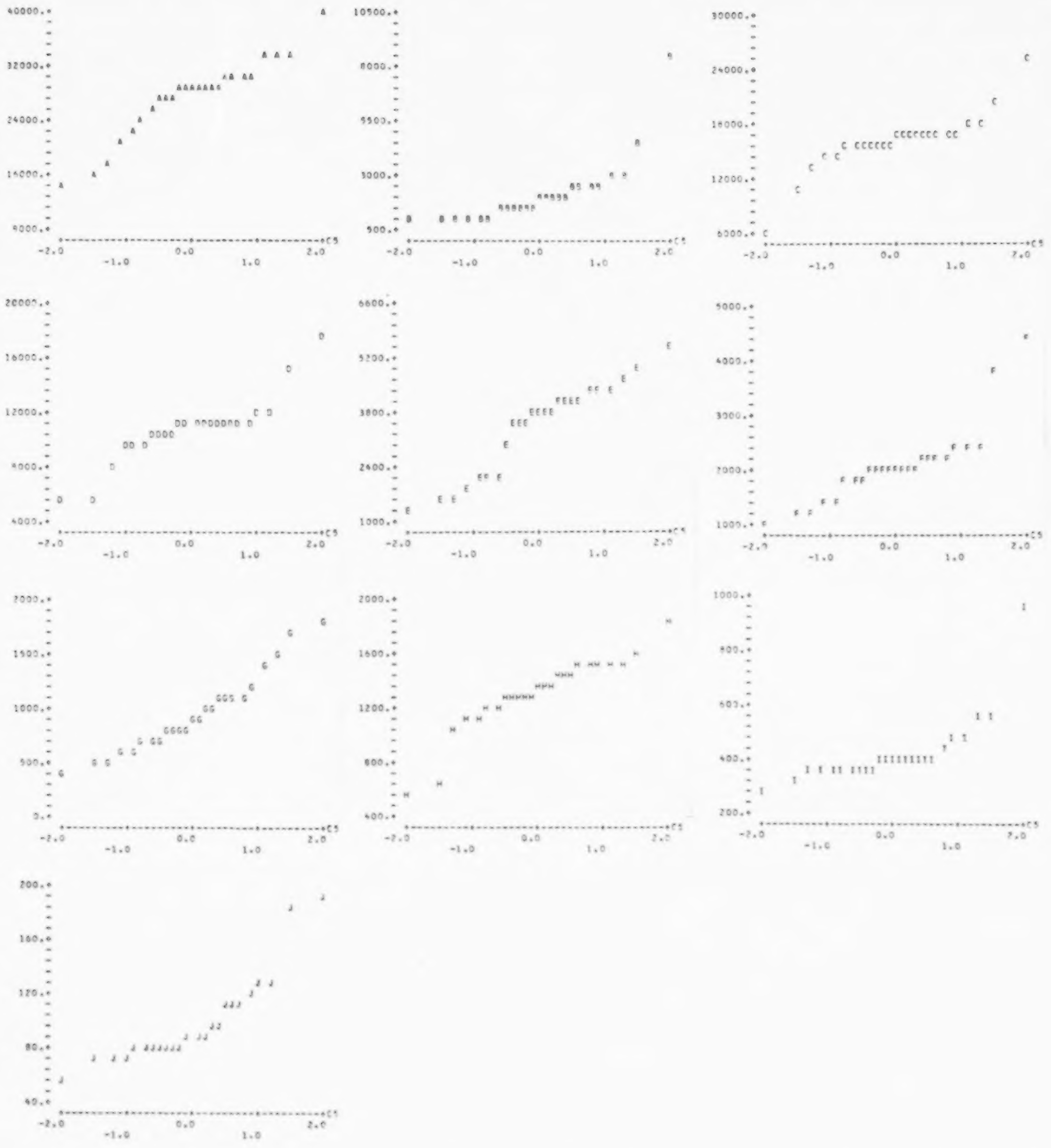

Figure 7.21. Ordered laboratory averages for COD data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

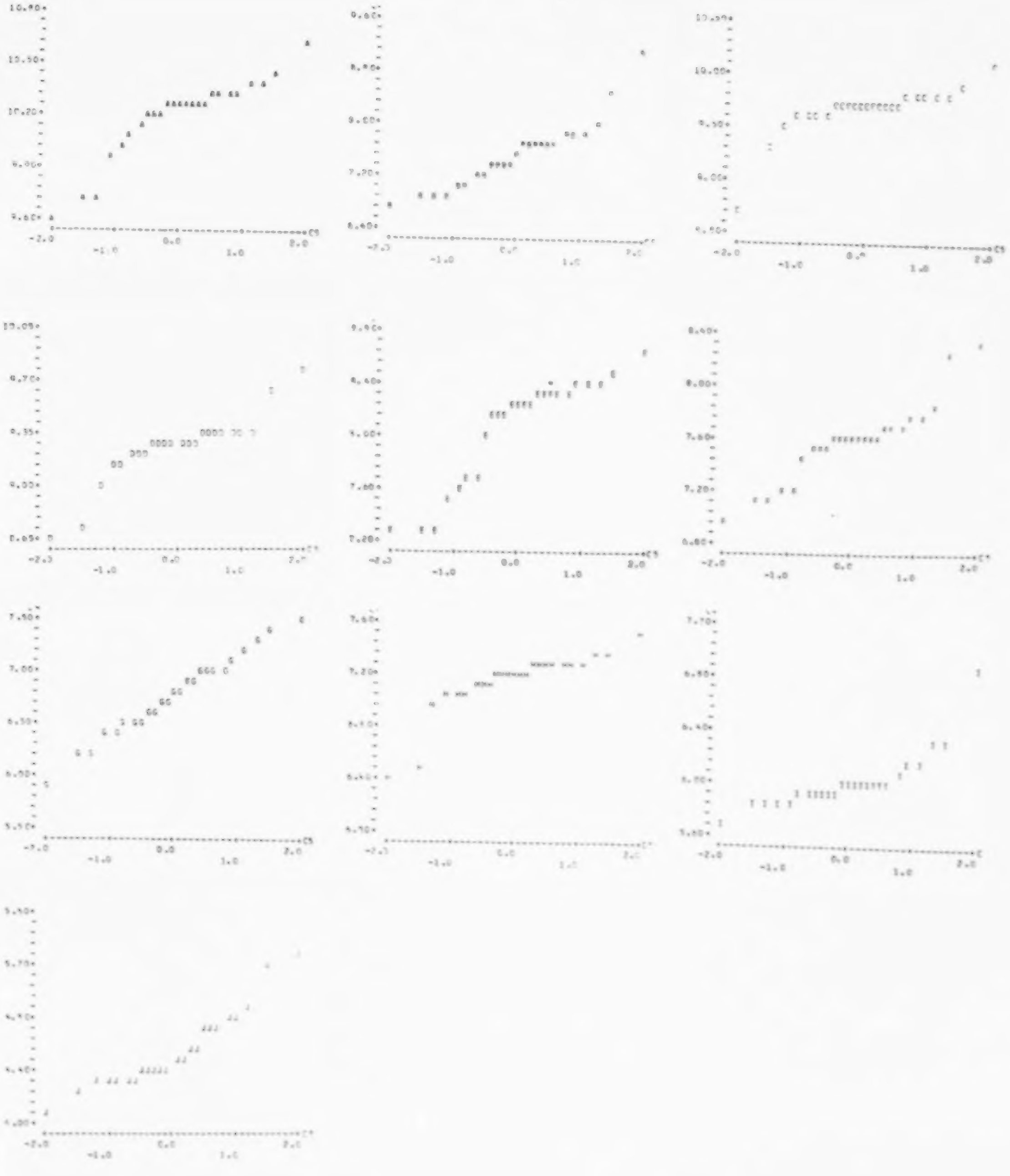

Figure 7.22. Ordered laboratory averages for $\log_e$ transformed COD data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

The data from 10 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.33. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction component estimates obtained for this data set are given in Table 7.34.

TABLE 7.33. ANALYSIS OF VARIANCE FOR LOG$_e$ COD DATA
BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	299	847.47544	--	--
Leachate Samples	9	828.15935	--	--
Laboratories	9	7.20557	.80062	5.77*
Lab x Sample	81	11.24247	.13380	32.0*
Residual	200	.86806	.00434	--

* $P < .005$

TABLE 7.34. VARIANCE COMPONENT ESTIMATES FOR LOG$_e$ COD DATA
BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.	Component	Estimate	95% Conf. Int.
σ^2_R	.0712	(.0492, .1124)	σ_R	.2669	(.2218, .3352)
σ^2_{LPLS}	.0669	(.0459, .1065)	σ_{LPLS}	.2586	(.2143, .3263)
σ^2_L	.0221	(.0092, .1046)	σ_L	.1485	(.0960, .3234)
σ^2_{LS}	.0448	(.0334, .0633)	σ_{LS}	.2117	(.1827, .2517)
σ^2_W	.0043	(.0036, .0053)	σ_W	.0659	(.0600, .0730)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.35. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.36.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .24$, $\sigma_L = .12$, and $\sigma = .20$. These values are smaller than the corresponding estimates given in Table 7.36, which indicates that greater precision may be attainable.

TABLE 7.35. ANALYSIS OF VARIANCE FOR LOG_e COD DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of squares	Mean Square	F
Total	249	689.8012	--	--
Leachate Samples	9	664.6838	--	--
Laboratories	24	11.1493	.4646	7.18*
Residual	216	13.9681	.0647	--

* $P < .005$

TABLE 7.36. VARIANCE COMPONENT ESTIMATES FOR LOG_e COD DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.1047	(.0812, .1402)	σ_R	.3236	(.2849, .3745)
σ^2_L	.0400	(.0227, .0881)	σ_L	.2000	(.1508, .2968)
σ^2*	.0647	(.0540, .0789)	σ**	.2544	(.2325, .2808)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

TOC Data Base

Data were received from 22 of the 34 laboratories that agreed to perform the TOC analysis. The analysis was performed in triplicate by 11 laboratories for all 10 leachate samples. A single value or an average value was reported by 8 laboratories. The remaining 3 laboratories reported an unequal number of replicates. One laboratory used 2 methods.

No values were reported as detection limits (i.e., < value) for this parameter, and no 0 mg/ℓ concentration levels were reported.

A summary of the analytical results for the 10 leachate samples is given in Table 7.37 . The average TOC concentration of the samples ranged from 61 to 9927 mg/ℓ, with the highest value generally 10 times larger than the lowest value for any particular leachate sample.

TABLE 7.37. SUMMARY OF ANALYTICAL RESULTS FOR TOC DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	9927	6100	20353	9498	425	2762
B	787	140	2207	693	106	456
C	5807	3700	12957	5645	294	1821
D	3457	2330	4500	3500	100	567
E	2220	170	22500	1273	133	4570
F	660	160	2053	618	34.5	376
G	413	80	1533	367	32.9	324
H	514	303	1700	445	18.1	323
I	299	26.7	1232	170	16.5	350
J	61	63.3	258	36	3.38	62.1

*All entries in mg/ℓ.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.23. A regression equation was calculated to be $\sigma = .0398\ \mu + 12.2$ with an R^2 value of 95%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .915 \log \mu - 1.04$ with an R^2 value of 93%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.71, 1.12), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

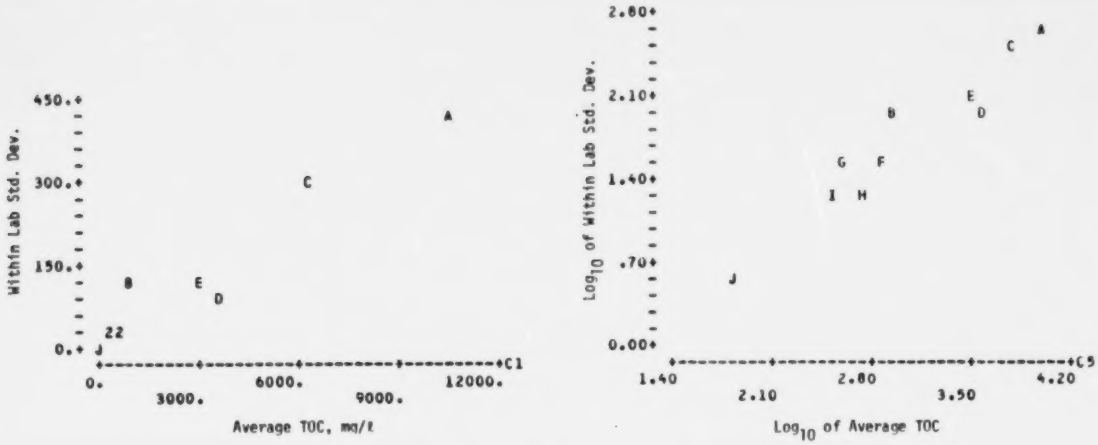

Figure 7.23. Relationship of the within laboratory standard deviation to the TOC concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.24. A regression equation was calculated to be $\sigma = .250\ \mu + 558$ with an R^2 value of 30%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .716 \log \mu + .627$ with an R^2 value of 77%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.39, 1.04), which suggests that a square root or logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. These transformed data were used in the statistical analysis of this parameter.

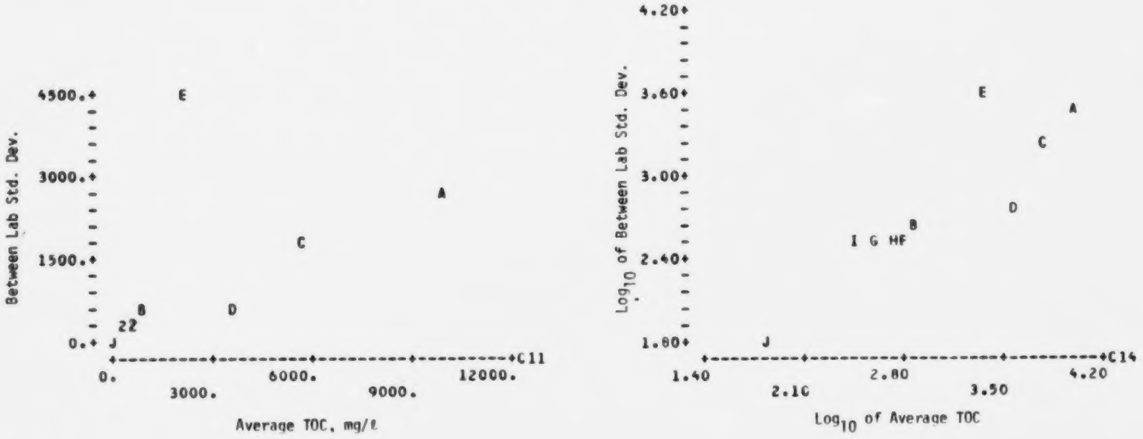

Figure 7.24. Relationship of the between laboratory standard deviation to the TOC concentration level.

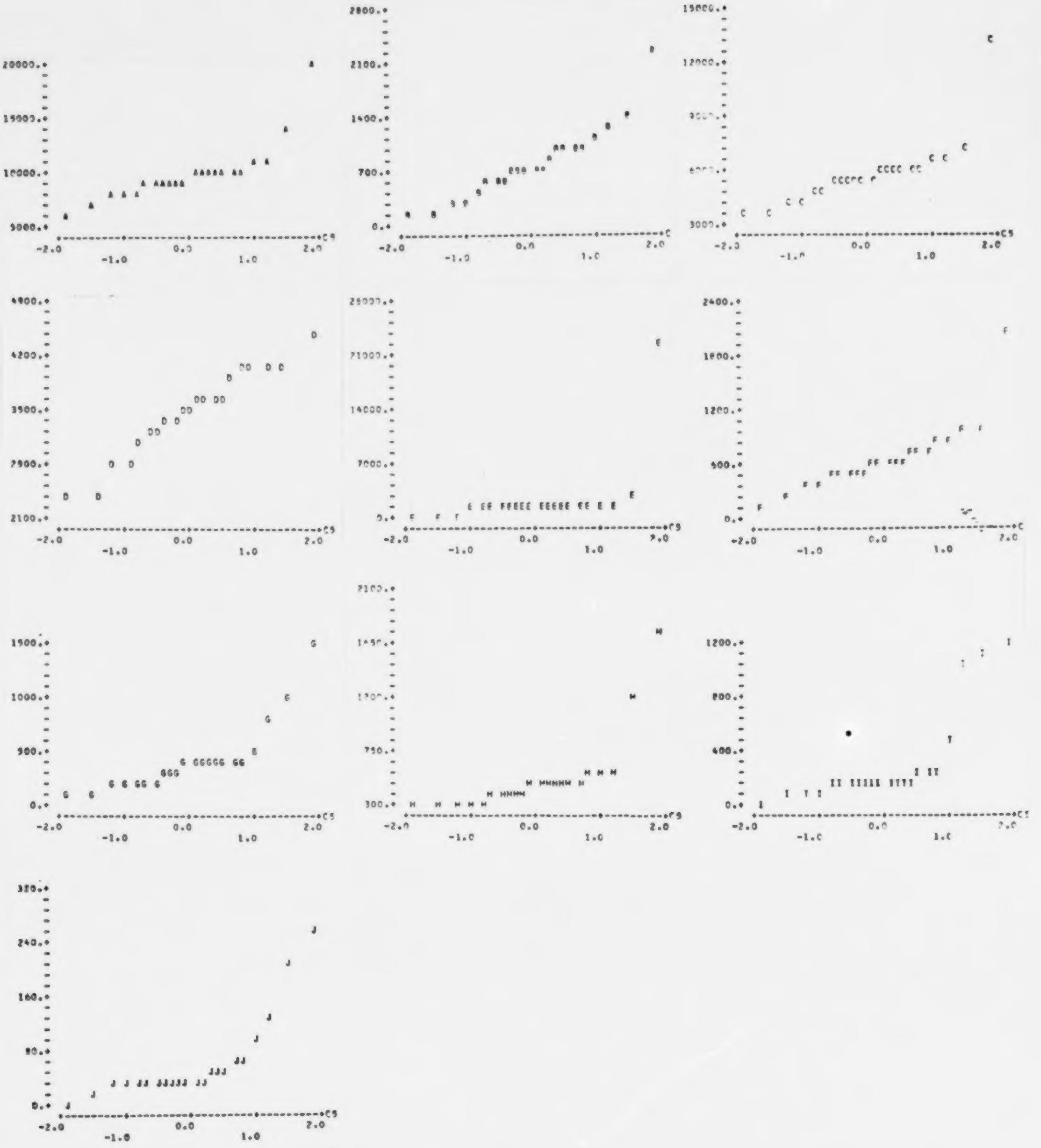

Figure 7.25. Ordered laboratory averages for TOC data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

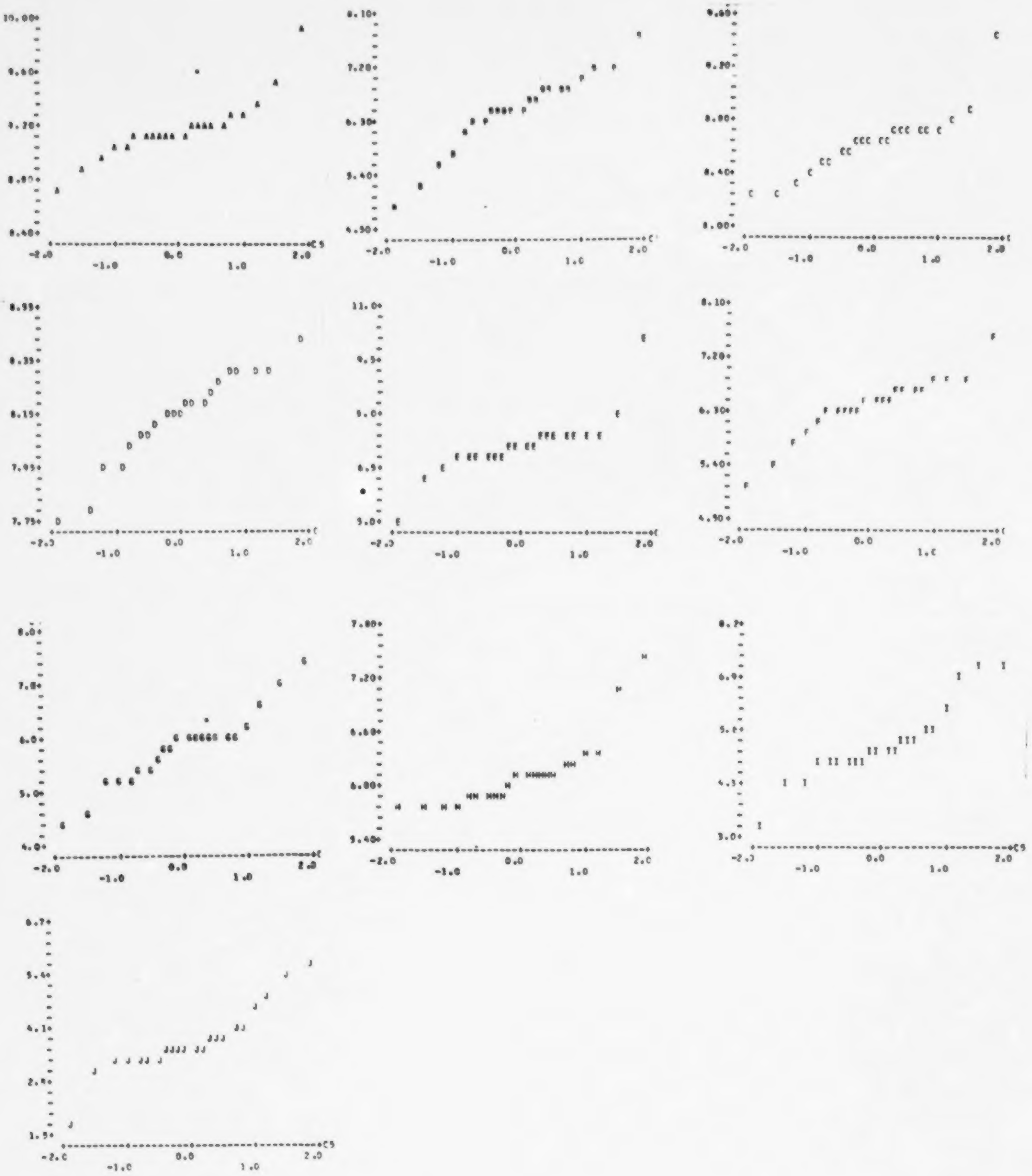

Figure 7.26. Ordered laboratory averages for $\log_e$ transformed TOC data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

The ordered laboratory averages for the TOC data plotted against the quantiles from a normal distribution are shown in Figure 7.25 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.26. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.38.

TABLE 7.38. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

	Leachate Sample											
Data	A	B	C	D	E	F	G	H	I	J	Average R^2	Std. dev. of R^2
Original	70	89	66	97	29	75	71	56	62	64	68	18
Transformed	84	93	83	95	75	93	94	77	89	88	87	7

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for 9 of the 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in some of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the log transformed TOC data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 11 laboratories were used to form a balanced data set. having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.39. The hypothesis that the between laboratory variance component is zero is not rejected. The hypothesis that the laboratory sample interaction variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.40.

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.41. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.42.

TABLE 7.39. ANALYSIS OF VARIANCE FOR LOG_e TOC DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	329	1004.4832	--	--
Leachate Samples	9	926.4478	--	--
Laboratories	10	10.8849	1.0885	1.48*
Lab x Sample	90	66.1043	.7345	153 **
Residual	220	1.0461	.0048	--

* .10 < P < .25

** P < .005

TABLE 7.40. VARIANCE COMPONENT ESTIMATES FOR LOG_e TOC DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.2598	(.2003, .3506)	σ_R	.5097	(.4476, .5921)
σ^2_{LPLS}	.2550	(.1961, .3454)	σ_{LPLS}	.5050	(.4428, .5877)
σ^2_L	.0118	(.0024, 11.4466)	σ_L	.1086	(.0485, 3.3833)
σ^2_{LS}	.2432	(.1850, .3342)	σ_{LS}	.4932	(.4301, .5781)
σ^2_W	.0048	(.0040, .0058)	σ_W	.0693	(.0634, .0764)

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .28$, $\sigma_L = .16$, and $\sigma = .24$. These values are smaller than the corresponding estimates given in Table 7.42, which indicates that greater precision may be attainable.

TABLE 7.41 ANALYSIS OF VARIANCE FOR LOG_e TOC DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	219	603.658	--	--
Leachate Samples	9	527.521	--	--
Laboratories	21	24.013	1.143	4.14*
Residual	189	52.124	.276	--

* $P < .005$

TABLE 7.42. VARIANCE COMPONENT ESTIMATES FOR LOG_e TOC DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.3627	(.2905, .4659)	σ_R	.6022	(.5389, .6825)
σ^2_L	.0867	(.0446, .2363)	σ_L	.2944	(.2111, .4861)
σ^2*	.2760	(.2278, .3413)	σ**	.5254	(.4773, .5842)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Total Residue Data Base

Data were received from 28 of the 45 laboratories that agreed to perform the total residue analysis. The analysis was performed in triplicate by 13 laboratories and in duplicate by 3 laboratories for all 10 leachate samples. A single value or an average value was reported by 9 laboratories. The remaining 3 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value) for this parameter, and no 0 mg/ℓ concentration levels were reported.

A summary of the analytical results for the 10 leachate samples is given in Table 7.43. The average total residue concentration of the samples ranged from 533 to 61,712 mg/ℓ, with the highest value generally 15 times larger than the lowest value for any particular leachate sample.

TABLE 7.43. SUMMARY OF ANALYTICAL RESULTS FOR TOTAL RESIDUE DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	61712	2310	108573	65252	3342	19798
B	6428	373	18293	6107	708	3221
C	15061	833	18219	15513	257	2951
D	7705	820	9137	7957	179	1479
E	4155	320	4913	4541	68.9	1076
F	2944	123	4433	3020	83.2	762
G	2831	197	3582	3094	155	725
H	1619	127	3960	1665	55.4	586
I	2780	290	3188	2932	57.3	559
J	533	73.3	844	542	23.7	113

*All entries in mg/ℓ

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.27. A regression equation was calculated to be $\sigma = .0529\ \mu - 76$ with an R^2 value of 95%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.01 \log \mu - 1.50$ with an R^2 value of 83%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.63, 1.38), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.28. A regression equation was calculated to be $\sigma = .320\ \mu - 255$ with an R^2 value of 98%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.03 \log \mu - .703$ with an R^2 value of 95%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.84, 1.23), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

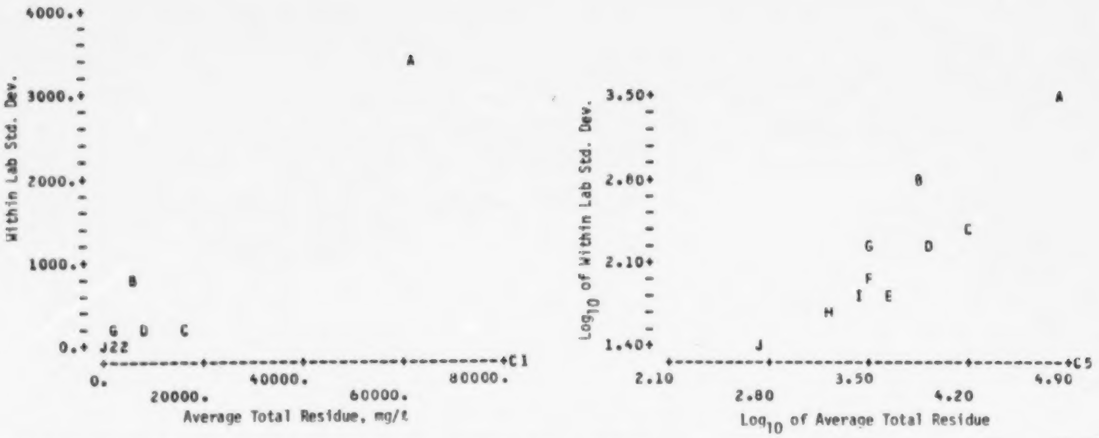

Figure 7.27. Relationship of the within laboratory standard deviation to the total residue concentration level.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. These transformed data were used in the statistical analysis of this parameter.

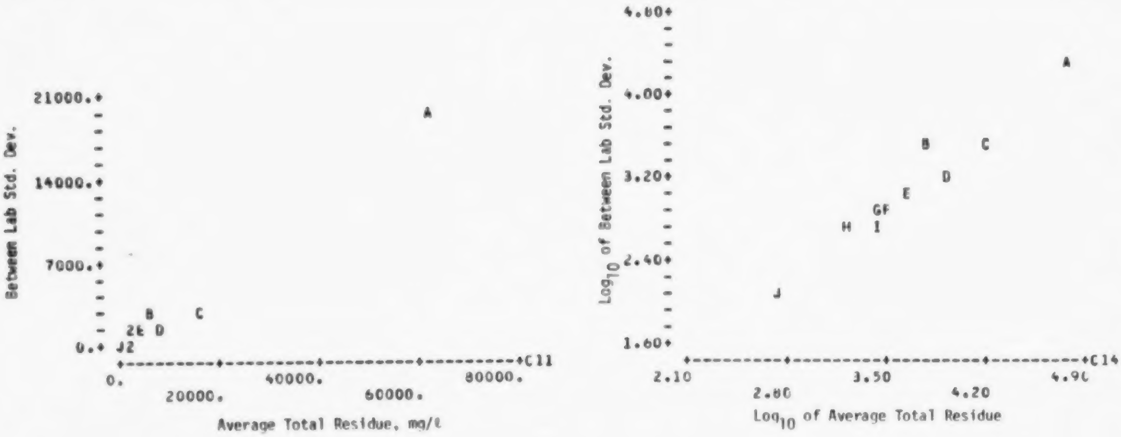

Figure 7.28. Relationship of the between laboratory standard deviation to the total residue concentration level.

The ordered laboratory averages for the total residue data plotted against the quantiles from a normal distribution are shown in Figure 7.29 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.30 . The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.44.

TABLE 7.44. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample A	B	C	D	E	F	G	H	I	J	Average R^2	Std. dev. of R^2
Original	62	79	45	50	61	72	73	62	47	60	61	11
Transformed	41	70	25	30	42	38	44	50	31	37	41	13

For the original data it appears that the distribution of the laboratory averages has a heavier lower tail than the lower tail of a normal distribution. The distribution of the $\log_e$ transformed data appears less similar to a normal distribution than the distribution of the original data (i.e., further from a straight line). This observation is supported by the lower R^2 values for all 10 leachate samples, the lower average R^2 , and greater standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples, however, which will affect the R^2 values for both the original and transformed data. Although the $\log_e$ transformed data were used in the statistical analysis of this parameter to stabilize the within and between laboratory variances, the logarithmic transformation does not appear to be appropriate to make the distribution of the data normal. Perhaps these data should be reanalyzed by converting the reported results into percentages of the sample average concentrations.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed total residue data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 13 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.45. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.46.

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.47. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.48.

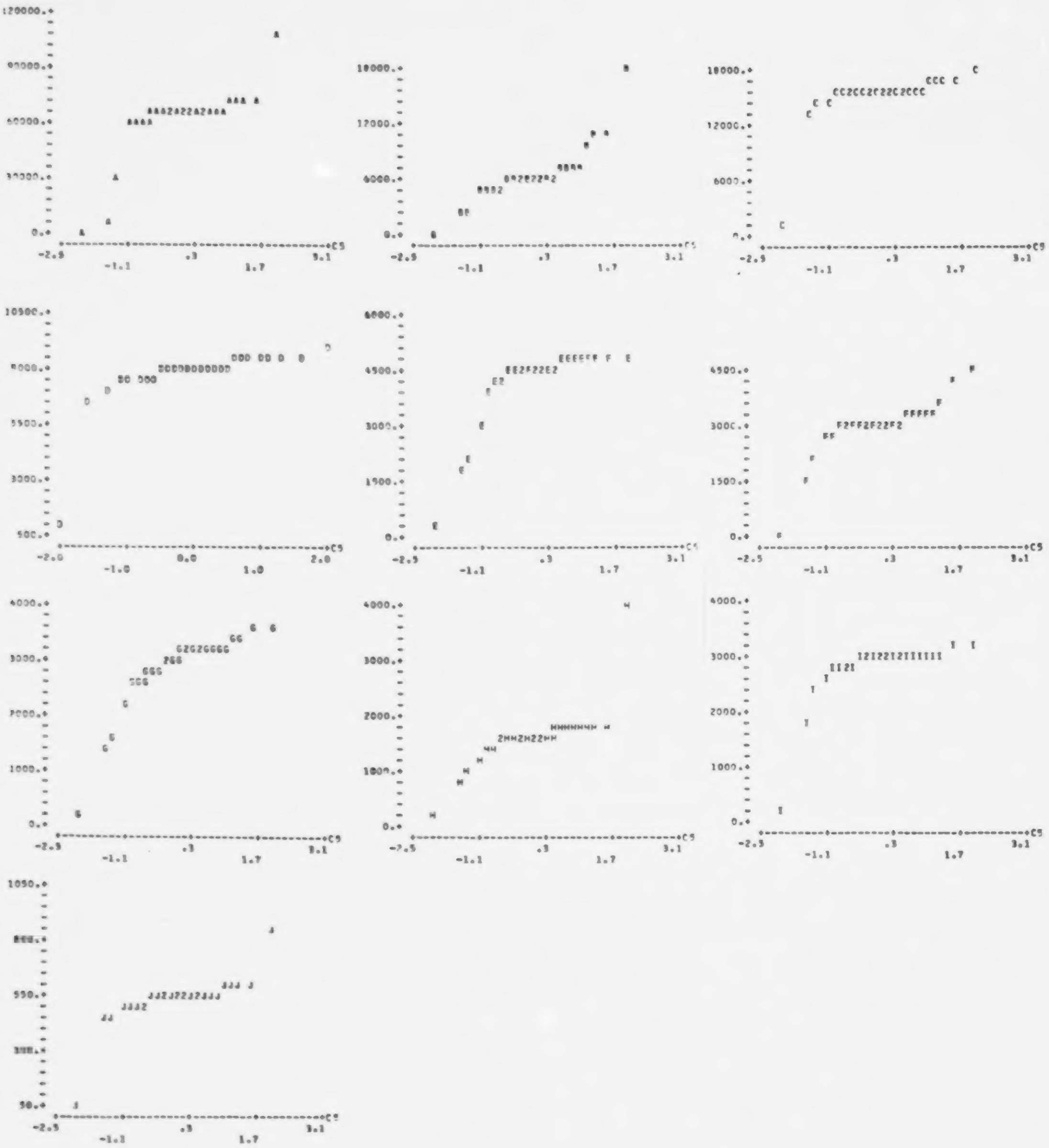

Figure 7.29. Ordered laboratory averages for total residue data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J,respectively.

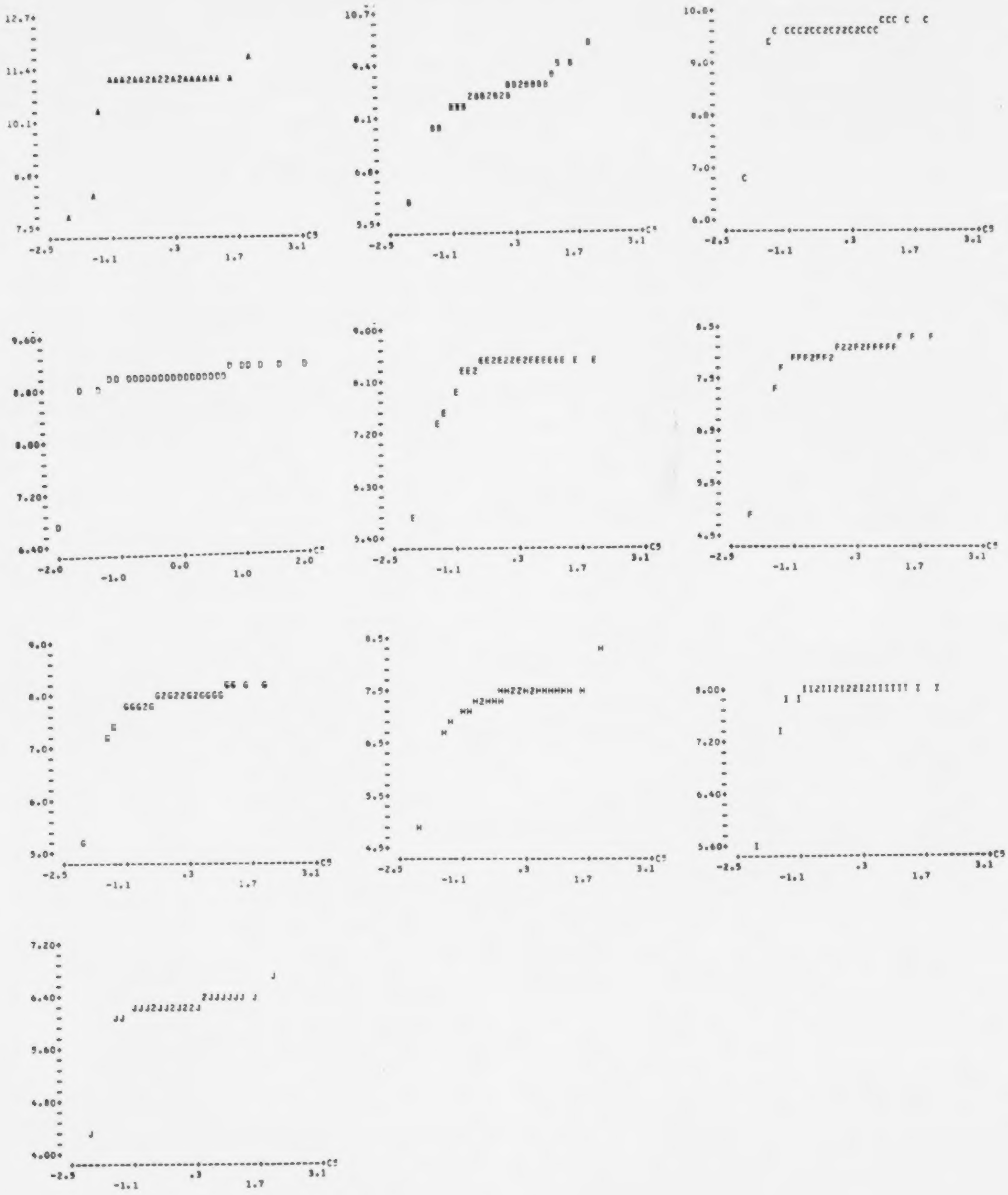

Figure 7.30 Ordered laboratory averages for $\log_e$ transformed total residue data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

TABLE 7.45. ANALYSIS OF VARIANCE FOR LOG_e TOTAL RESIDUE DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	389	792.33062		
Leachate Samples	9	573.00535		
Laboratories	12	206.90451	17.24204	163*
Lab x Sample	108	11.43357	.10587	27.9*
Residual	260	.98719	.00380	

* $P < .005$

TABLE 7.46. VARIANCE COMPONENT ESTIMATES FOR LOG_e TOTAL RESIDUE DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.6090	(.3230, 1.5496)	σ_R	.7804	(.5683, 1.2448)
σ^2_{LPLS}	.6052	(.3199, 1.5509)	σ_{LPLS}	.7780	(.5656, 1.2453)
σ^2_L	.5712	(.2926, 1.5693)	σ_L	.6558	(.5409, 1.2527)
σ^2_{LS}	.0340	(.0263, .0458)	σ_{LS}	.1845	(.1621, .2141)
σ^2_W	.0038	(.0032, .0045)	σ_W	.0616	(.0568, .0674)

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .21$, $\sigma_L = .13$, and $\sigma = .16$. These values are smaller than the corresponding estimates given in Table 7.48, which indicates that greater precision may be attainable.

TABLE 7.47. ANALYSIS OF VARIANCE FOR LOG_e TOTAL RESIDUE DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	279	492.6379	--	--
Leachate Samples	9	403.7872	--	--
Laboratories	27	73.8334	2.7346	44.2*
Residual	243	15.0173	.0618	--

* $P < .005$

TABLE 7.48. VARIANCE COMPONENT ESTIMATES FOR LOG_e TOTAL RESIDUE DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.3291	(.2207, .5430)	σ_R	.5737	(.4698, .7369)
σ^2_L	.2673	(.1654, .5037)	σ_L	.5170	(.4067, .7097)
σ^2*	.0618	(.0521, .0744)	σ**	.2486	(.2283, .2729)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Volatile Residue Data Base

Data were received from 27 of the 41 laboratories that agreed to perform the volatile residue analysis. The analysis was rpeformed in triplicate by 11 laboratories and in duplicate by 2 laboratories for all 10 leachate samples. A single value or an average value was reported by 9 laboratories. The remaining 5 laboratories reported an unequal number of replicates.

No values were reported as dectection limits (i.e., < value) for this parameter, and 0 mg/ℓ concentration levels occurring in leachate sample G were reported by one laboratory.

A summary of the analytical results for the 10 leachate samples is given in Table 7.49 . The average volatile residue concentration of the samples ranged from 138 to 16,846 mg/ℓ, with the highest value generally 30 times larger than the lowest value for any particular leachate sample.

TABLE 7.49. SUMMARY OF ANALYTICAL RESULTS FOR VOLATILE RESIDUE DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	16846	391	83500	12175	3016	16312
B	1793	180	6188	1699	184	1056
C	6393	277	11010	6533	281	1618
D	3096	283	5375	3100	162	807
E	2168	133	5989	2235	1649	1021
F	1425	11	3703	1400	56	585
G	919	0	2668	823	102	493
H	677	50	1491	676	85.7	259
I	827	147	2296	746	77.3	397
J	138	102	568	116	17.1	102

* All entries in mg/ℓ

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.31 . A regression equation was calculated to be $\sigma = .15\ \mu + 7$ with an R^2 value of 74%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .995 \log \mu - .980$ with an R^2 value of 71%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.48, 1.51), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

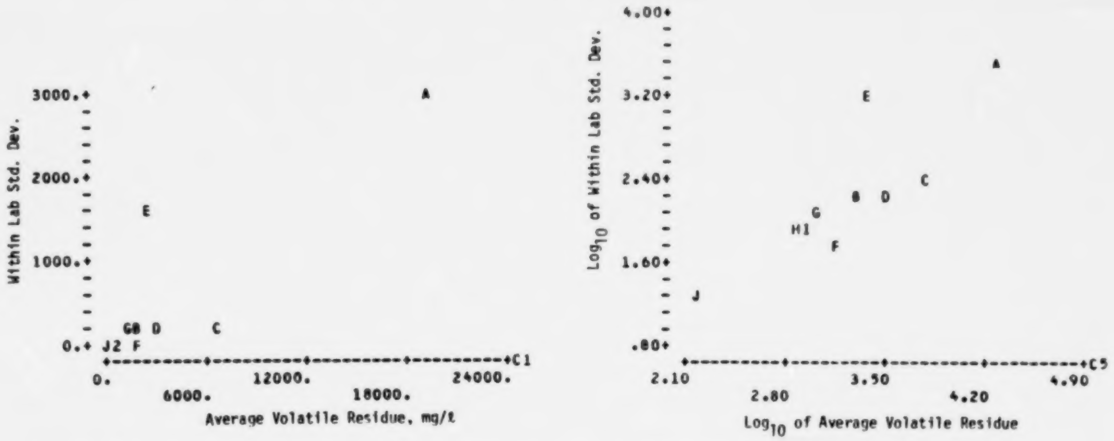

Figure 7.31 . Relationship of the within laboratory standard deviation to the volatile residue concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.32. A regression equation was calculated to be $\sigma = .944\ \mu - 972$ with an R^2 value of 92%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .966 \log \mu - .219$ with an R^2 value of 90%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.70, 1.23), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

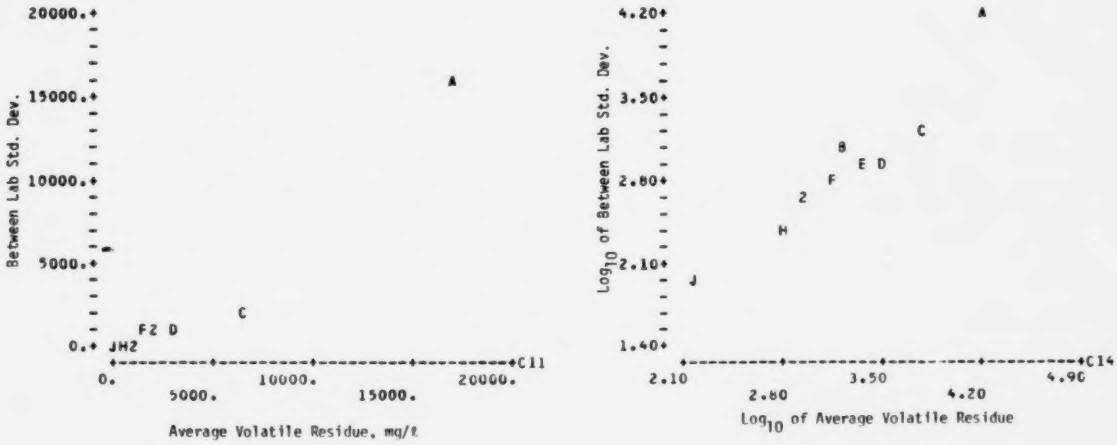

Figure 7.32 Relationship of the between laboratory standard deviation to the volatile residue concentration level.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, 4 was added to all zero (0) values. These transformed data were used in the statistical analysis of this parameter.

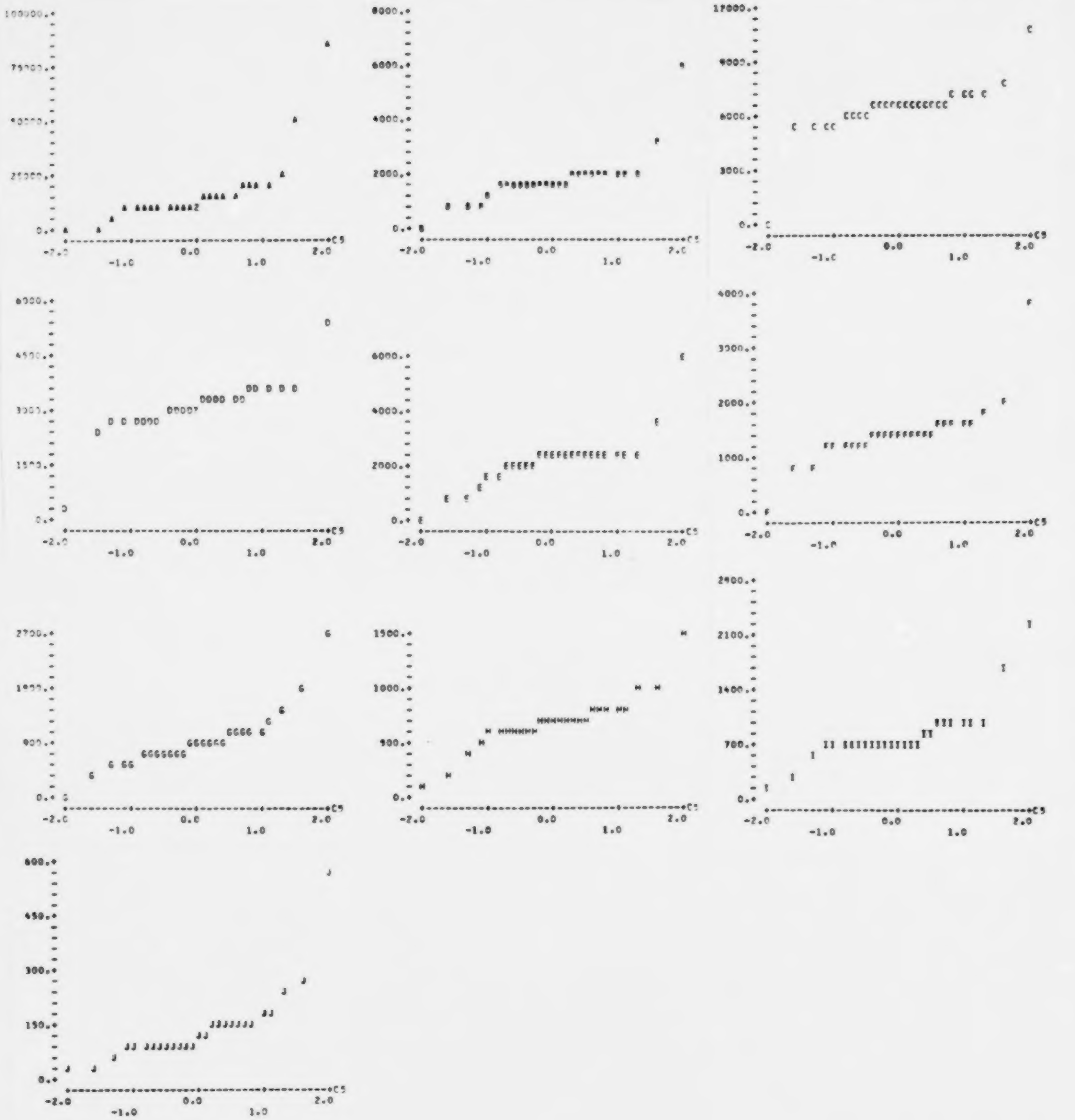

Figure 7.33. Ordered laboratory averages for volatile residue data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J,respectively.

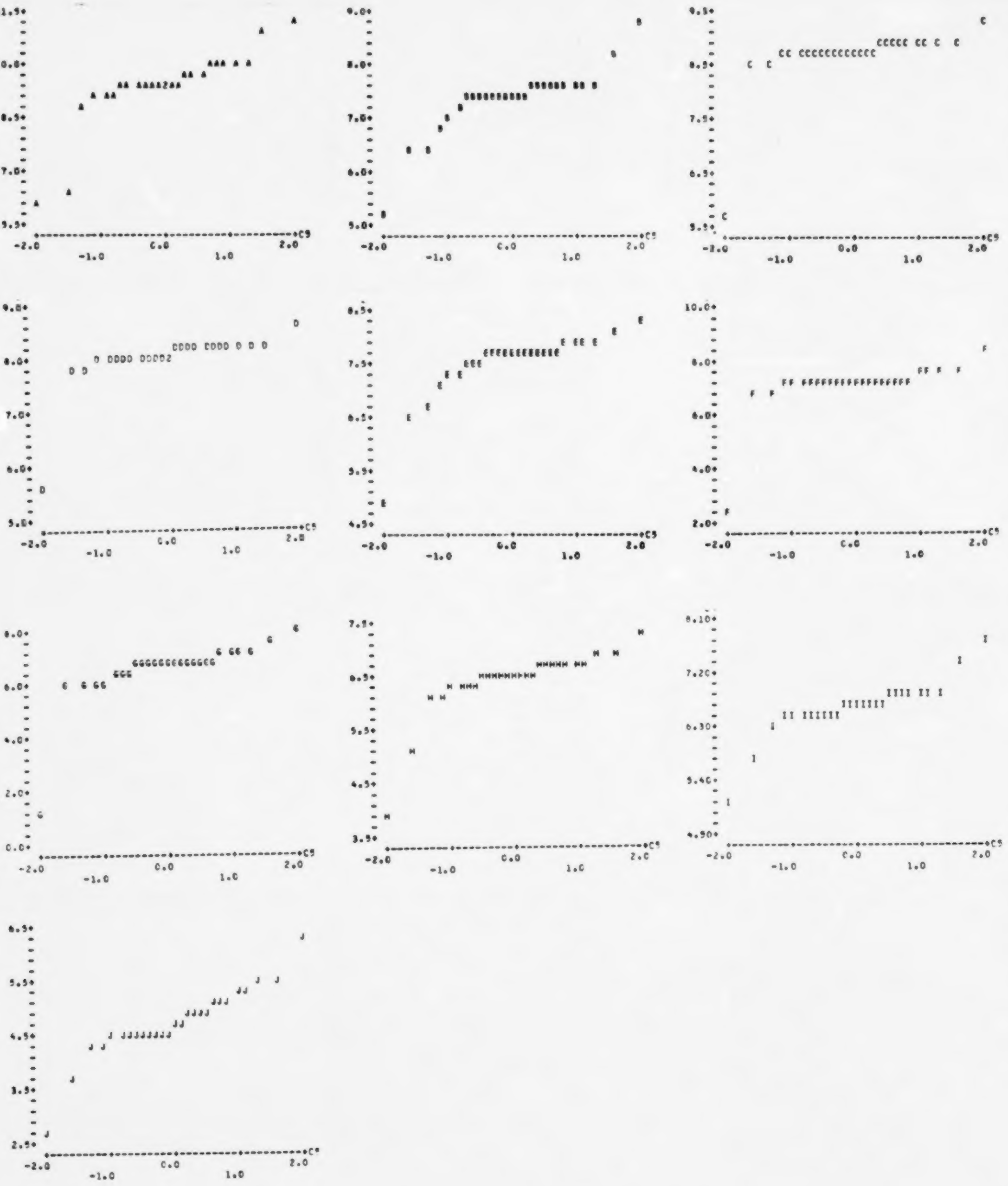

Figure 7.34. Ordered laboratory averages for $\log_e$ transformed volatile residue data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

The ordered laboratory averages for the volatile residue data plotted against the quantiles from a normal distribution are shown in Figure 7.33 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.34. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.50.

TABLE 7.50. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

	Leachate Sample										Average	Std. dev.
Data	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	59	65	68	76	75	72	84	86	72	67	72	8
Transformed	70	75	35	45	63	39	51	63	79	88	61	18

For the original data it appears that the distribution of the laboratory averages has a slightly heavier lower tail and a heavier upper tail than the lower and upper tails of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e.,closer to a straight line). The lower R^2 values for 6 of the 10 leachate samples, the lower average R^2 , and greater standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data appears to be caused by outlying averages. Several outlying averages are present in most of the leachate samples which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed volatile residue data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 11 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.51. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.52.

TABLE 7.51. ANALYSIS OF VARIANCE FOR LOG_e VOLATILE RESIDUE DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	329	850.6597	--	--
Leachate Samples	9	484.22	--	--
Laboratories	10	302.7444	30.2744	47.6*
Lab x Sample	90	57.2337	.6359	21.6*
Residual	220	6.4616	.0294	--

* $P < .005$

TABLE 7.52. VARIANCE COMPONENT ESTIMATES FOR LOG_e VOLATILE RESIDUE DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.2195	(.6599, 2.9717)	σ_R	1.1043	(.8123, 1.7239)
σ^2_{LPLS}	1.1901	(.6358, 2.9801)	σ_{LPLS}	1.0909	(.7974, 1.7263)
σ^2_L	.9880	(.4761, 3.1412)	σ_L	.9940	(.6900, 1.7724)
σ^2_{LS}	.2022	(.1521, .2819)	σ_{LS}	.4496	(.3900, .5309)
σ^2_W	.0294	(.0246, .0358)	σ_W	.1715	(.1568, .1891)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.53. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.54.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .29$, $\sigma_L = .18$, and $\sigma = .22$. These values are considerably smaller than the corresponding estimates given in Table 7.54, which indicates that greater precision may be attainable.

TABLE 7.53. ANALYSIS OF VARIANCE FOR LOG_e VOLATILE RESIDUE DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	269	556.215	--	--
Leachate Samples	9	404.682	--	--
Laboratories	26	110.453	4.248	24.1*
Residual	234	41.081	.176	--

* $P < .005$

TABLE 7.54. VARIANCE COMPONENT ESTIMATES FOR LOG_e VOLATILE RESIDUE DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.5832	(.4059, .9093)	σ_R	.7637	(.6371, .9536)
σ^2_L	.4072	(.2479, .7898)	σ_L	.6381	(.4979, .8887)
σ^2*	.1760	(.1480, .2128)	σ**	.4195	(.3847, .4613)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Organic Nitrogen Data Base

Data were received from 18 of the 38 laboratories that agreed to perform the organic nitrogen analysis. The analysis was performed in triplicate by 7 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 6 laboratories. The remaining 4 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value) for this parameter, and five 0 mg/ℓ concentration levels in leachate samples B, G, H, and J with frequency 1, 1, 1, and 2, respectively, were reported. Five laboratories reported one or more zero concentration levels.

A summary of the analytical results for the 10 leachate samples is given in Table 7.55 . The average organic nitrogen concentration of the samples ranged from 8.89 to 457 mg/ℓ, with the highest value generally 100 times larger than the lowest value for any particular leachate sample.

TABLE 7.55. SUMMARY OF ANALYTICAL RESULTS FOR ORGANIC NITROGEN DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	457	8.66	906	330	27.1	282
B	97.3	0	900	31.1	11.3	113
C	416	11.5	1100	140	22.2	415
D	204	2.75	595	77.2	15.0	212
E	168	2.36	1654	56.2	22.2	375
F	107	5.78	832	59.6	13.5	182
G	53.5	0	170	27.5	14.5	52
H	16.2	1	49.4	8.82	1.53	14.1
I	67.5	0	277	17.3	9.12	97.7
J	8.89	0.133	22.1	5.17	3.04	8.16

*All entries in mg/ℓ.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.35 . A regression equation was calculated to be $\sigma - .0535 \mu + 5.64$ with an R^2 value of 84%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .680 \log \mu - .309$ with an R^2 value of 84%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.44, .92), which suggests that a square root or perhaps a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, .1 was added to all zero values. These transformed data were used in the statistical analysis of this parameter.

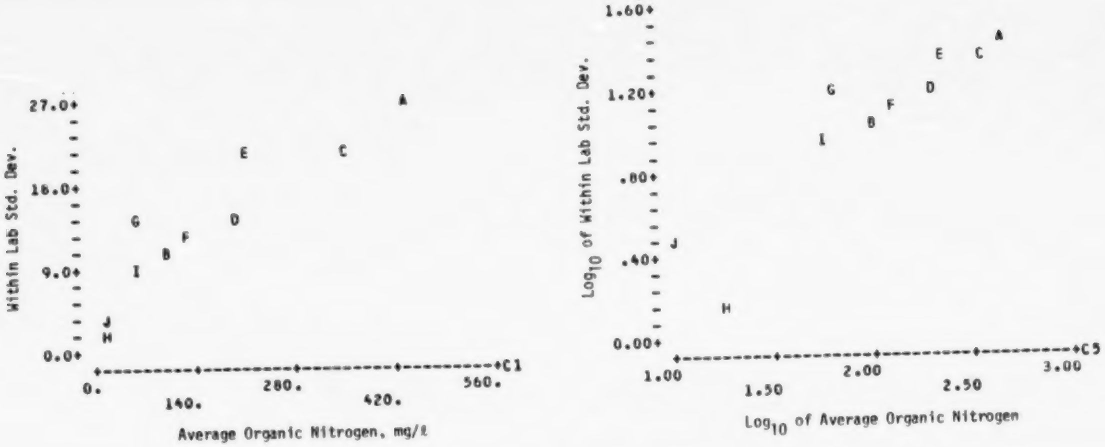

Figure 7.35. Relationship of the within laboratory standard deviation to the organic nitrogen concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.36. A regression equation was calculated to be $\sigma = .746\ \mu + 56$ with an R^2 value of 67%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.01 \log \mu + .025$ with an R^2 value of 93%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.78, 1.25), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

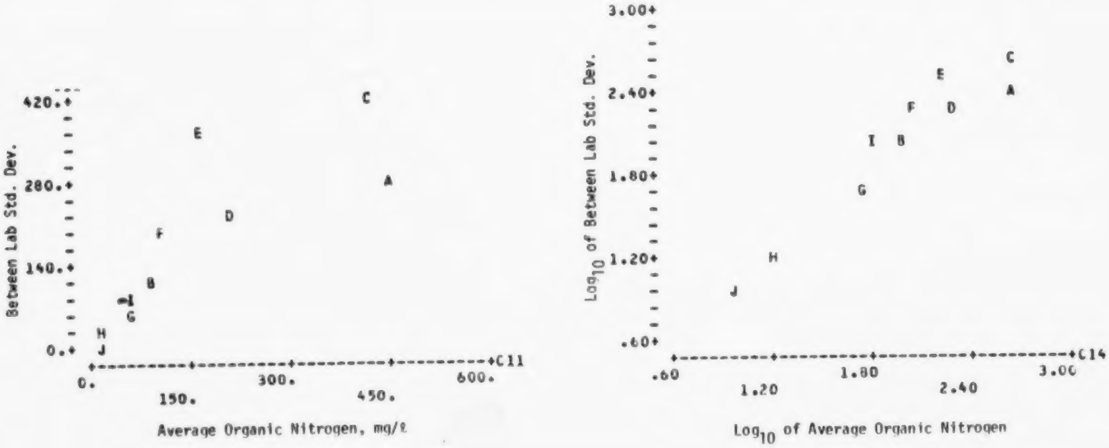

Figure 7.36. Relationship of the between laboratory standard deviation to the organic nitrogen concentration level.

The ordered laboratory averages for the organic nitrogen data plotted against the quantiles from a normal distribution are shown in Figure 7.37 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.38. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.56.

TABLE 7.56. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

	Leachate Sample											
Data	A	B	C	D	E	F	G	H	I	J	Average R^2	Std. dev. of R^2
Original	90	76	81	82	34	33	86	83	68	82	72	21
Transformed	71	83	92	92	83	69	85	92	92	91	85	9

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e. closer to a straight line). This observation is supported by the higher R^2 values for 8 of the 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in some of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed organic nitrogen data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 7 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.57. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance components estimates obtained for this data set are given in Table 7.58.

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.59. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.60.

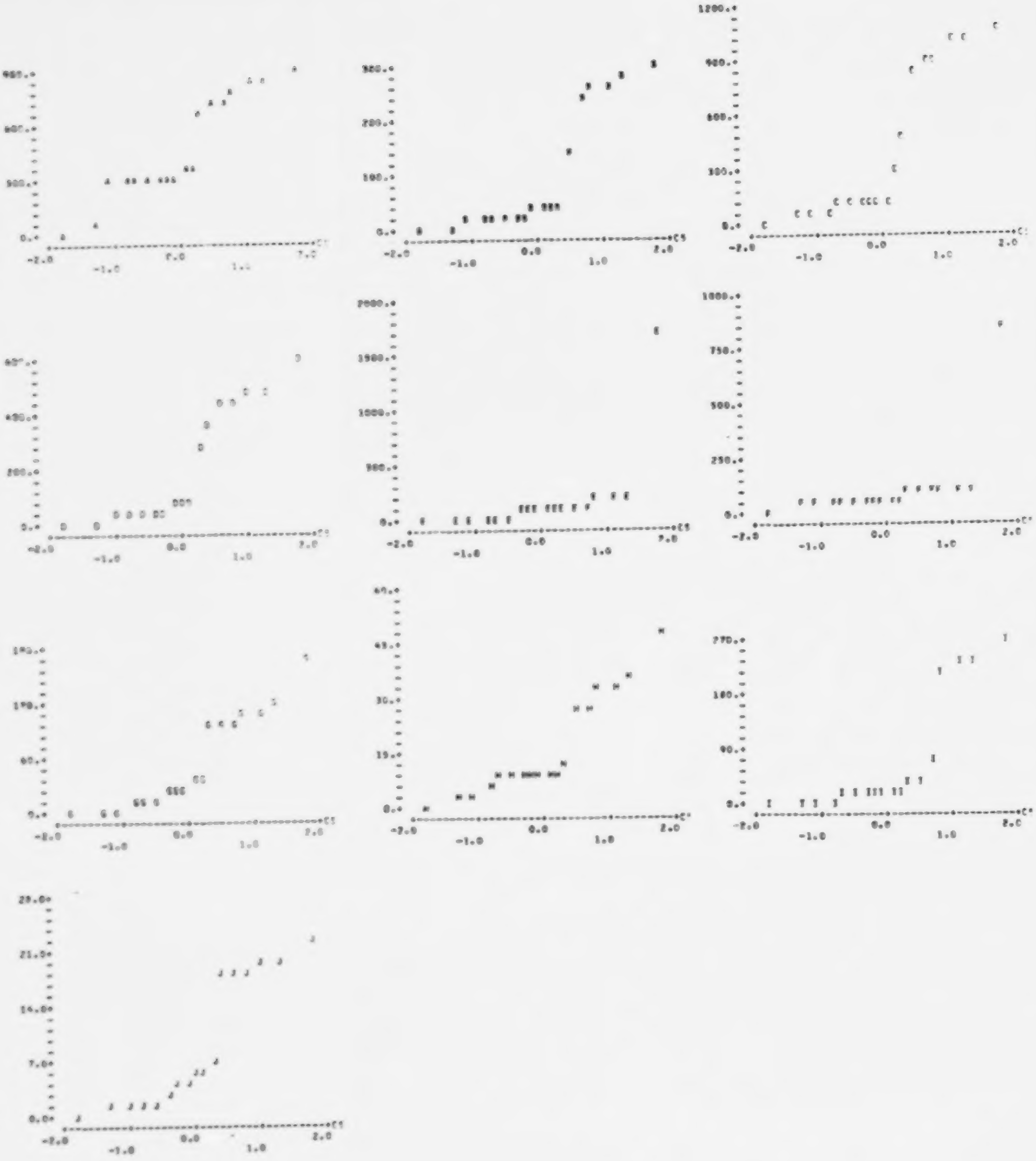

Figure 7.37. Ordered laboratory averages for organic nitrogen data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

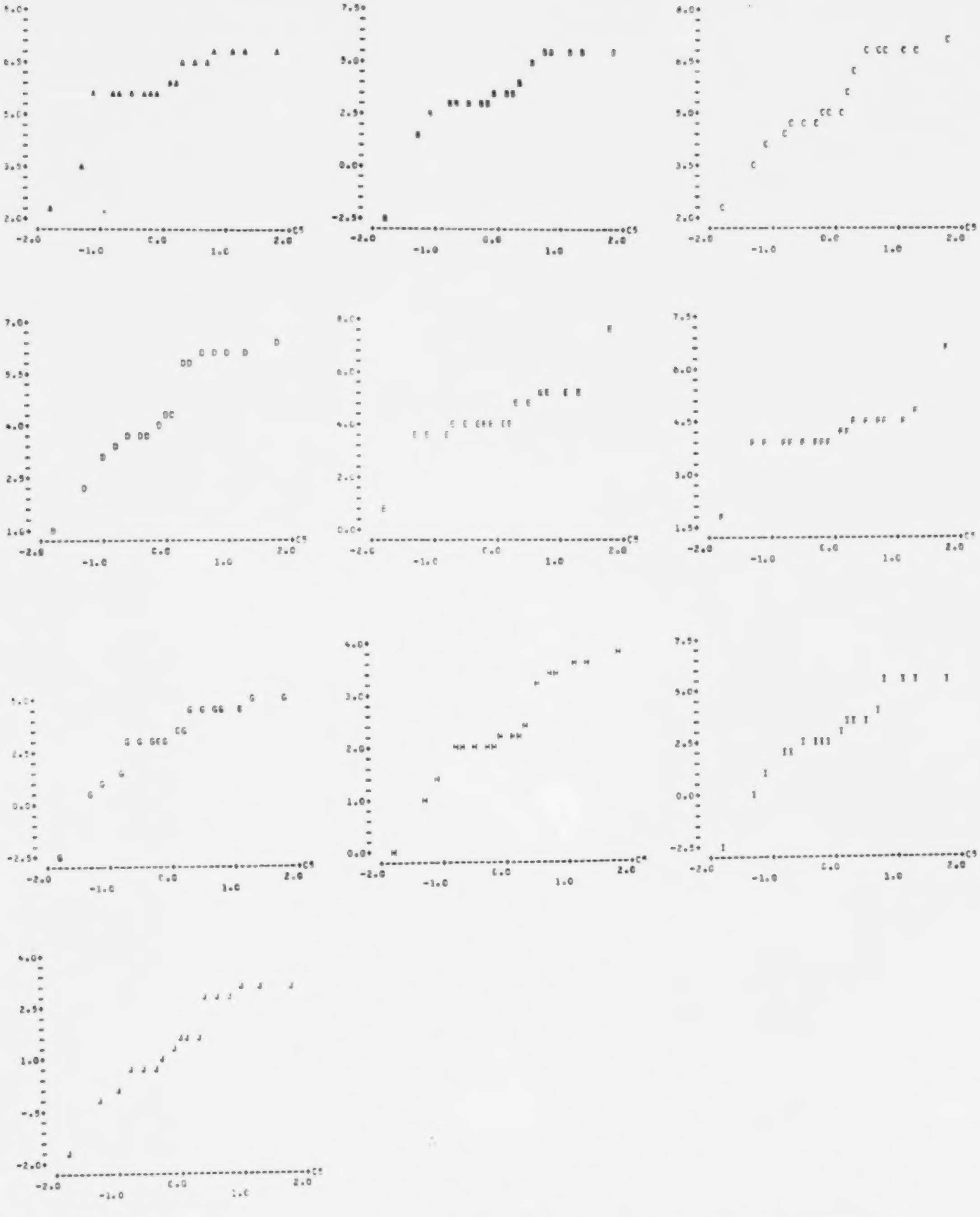

Figure 7.38. Ordered laboratory averages for $\log_e$ transformed organic nitrogen data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

TABLE 7.57. ANALYSIS OF VARIANCE FOR LOG_e ORGANIC NITROGEN DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	209	580.249	--	--
Leachate Samples	9	332.9673	--	--
Laboratories	6	160.7284	26.7881	18.9*
Lab x Sample	54	76.6932	1.4202	20.2*
Residual	140	9.8600	.0704	--

* P < .005

TABLE 7.58. VARIANCE COMPONENT ESTIMATES FOR LOG_e ORGANIC NITROGEN DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.3659	(.7273, 3.4459)	σ_R	1.1687	(.8528, 1.8563)
σ^2_{LPLS}	1.2955	(.6708, 3.4752)	σ_{LPLS}	1.1382	(.8190, 1.8642)
σ^2_L	.3379	(.3379, 4.6483)	σ_L	.9196	(.5813, 2.1560)
σ^2_{LS}	.4499	(.3137, .6998)	σ_{LS}	.6708	(.5601, .8365)
σ^2_W	.0704	(.0564, .0903)	σ_W	.2653	(.2376, .3005)

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .93$, $\sigma_L = .76$, and $\sigma - .53$. These values are smaller than the corresponding estimates given in Table 7.60, which indicates that greater precision may be attainable.

TABLE 7.59. ANALYSIS OF VARIANCE FOR LOG_e ORGANIC NITROGEN DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	179	666.02	--	--
Leachate Samples	9	285.34	--	--
Laboratories	17	198.58	11.68	9.82*
Residual	153	182.10	1.19	--

* $P < .005$

TABLE 7.60. VARIANCE COMPONENT ESTIMATES FOR LOG_e ORGANIC NITROGEN DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	2.2390	(1.6008, 3.3551)	σ_R	1.4963	(1.2652, 1.8317)
σ^2_L	1.0490	(.5588, 2.6436)	σ_L	1.0242	(.7475, 1.6259)
σ^2*	1.1900	(.9626, 1.5092)	σ**	1.0909	(.9811, 1.2285)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Ammonia Nitrogen Data Base

Data were received from 25 of the 46 laboratories that agreed to perform the ammonia nitrogen analysis. The analysis was performed in triplicate by 11 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 8 laboratories. The remaining 5 laboratories reported an unequal number of replicates.

Three values of 3 mg/ℓ were reported as detection limits (i.e., < value). Half the reported detection limit value was used in the data base for all statistical analyses. No 0 mg/ℓ concentration levels were reported.

A summary of the analytical results for the 10 leachate samples is given in Table 7.61. The average ammonia nitrogen concentration of the samples ranged from 17.7 to 799 mg/ℓ, with the highest value generally 100 times larger than the lowest value for any particular leachate sample.

TABLE 7.61. SUMMARY OF ANALYTICAL RESULTS FOR AMMONIA NITROGEN DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	408	4.97	825	411	21.5	170
B	204	2.30	330	216	12.1	71.5
C	799	8.27	1800	835	32.4	341
D	389	4.5	725	420	31.6	165
E	103	1.2	165	103	6.65	33.5
F	38.2	3.15	263	28	2.73	49.5
G	76.6	.933	136	82.3	5.44	31.8
H	24.9	2.5	60	23.6	.97	11.3
I	213	13.4	533	218	6.85	98.7
J	17.7	1.5	50	16.3	2.07	9.61

* All entries in mg/ℓ.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.39. A regression equation was calculated to be $\sigma = .047\ \mu + 1.99$ with an R^2 value of 85%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .861 \log \mu - .920$ with an R^2 value of 90%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.63, 1.09), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

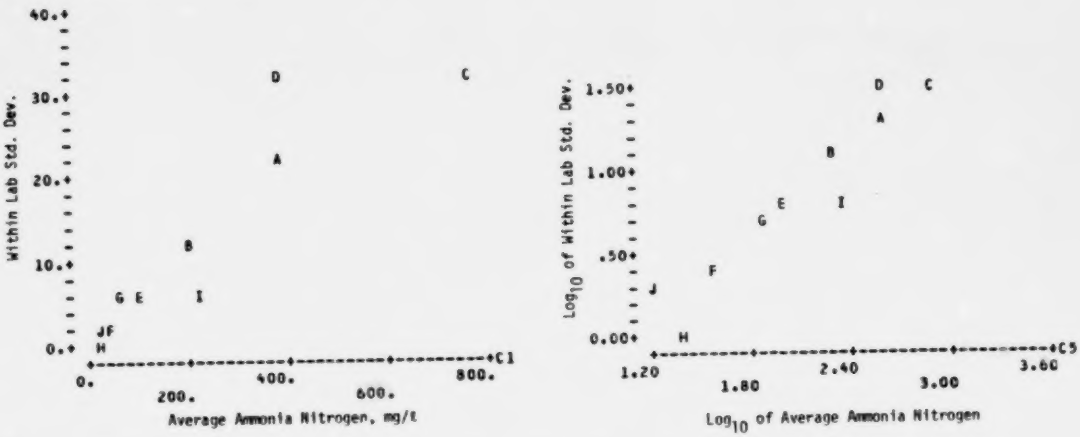

Figure 7.39. Relationship of the within laboratory standard deviation to the ammonia nitrogen concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.40. A regression equation was calculated to be $\sigma = .415\ \mu + 3.69$ with an R^2 value of 99%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .872 \log \mu - .061$ with an R^2 value of 91%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.65, 1.09), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

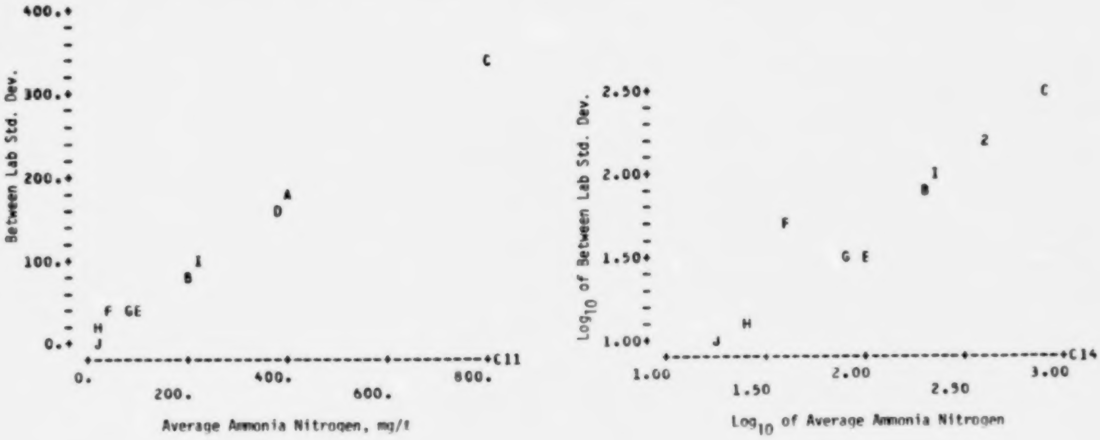

Figure 7.40. Relationship of the between laboratory standard deviation to the ammonia nitrogen concentration level.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. These transformed data were used in the statistical analysis of this parameter.

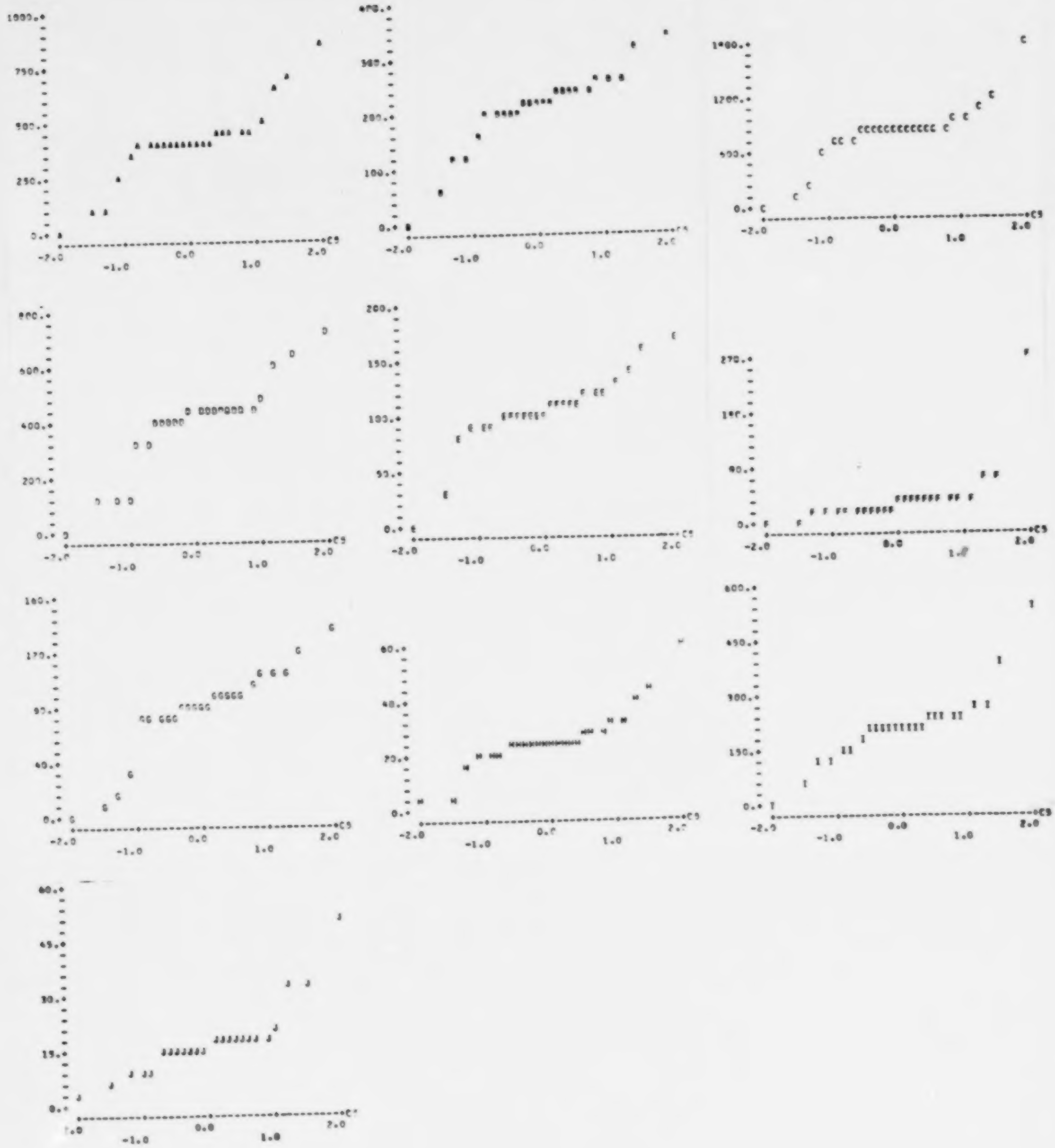

Figure 7.41. Ordered laboratory averages for ammonia nitrogen data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

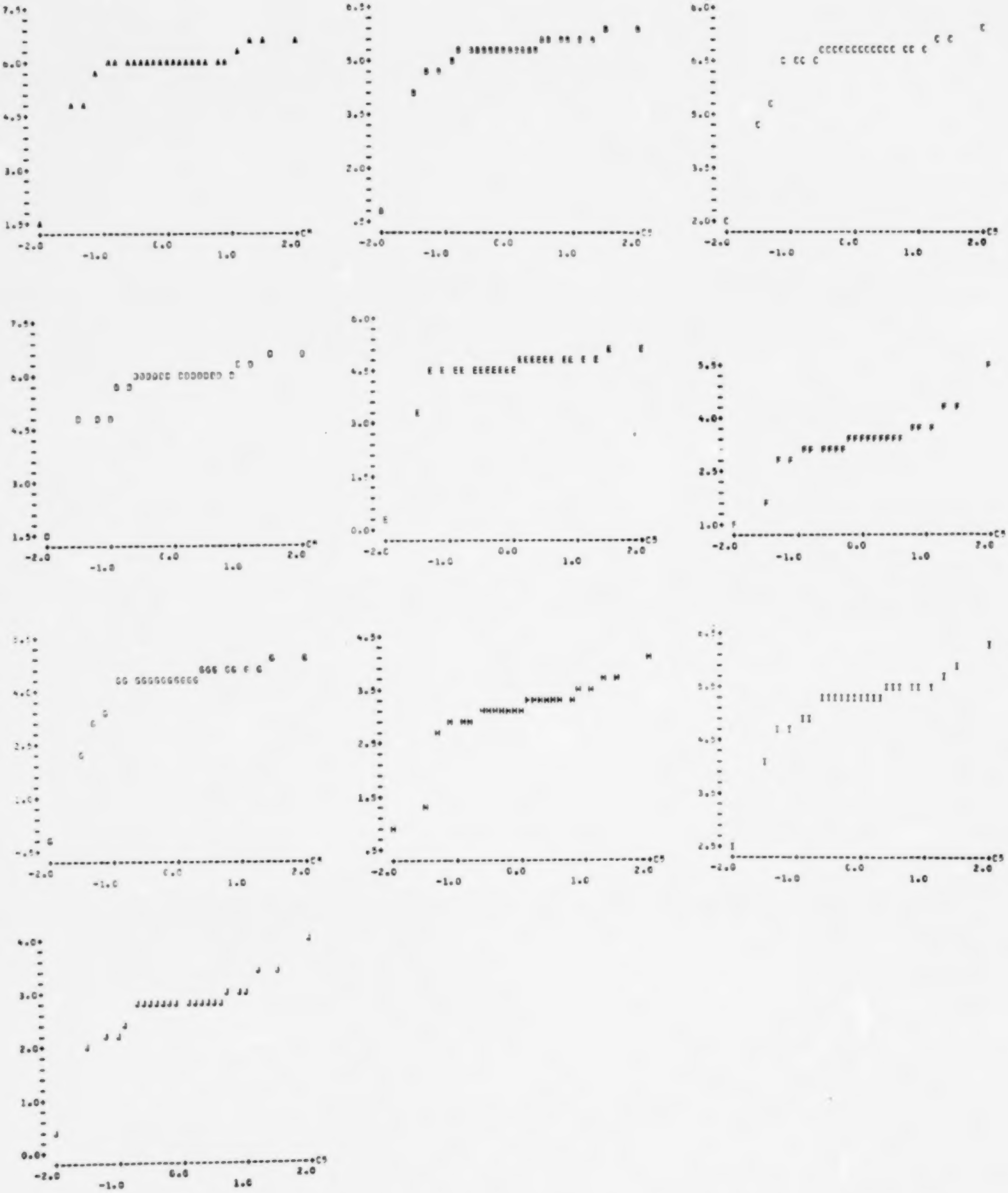

Figure 7.42. Ordered laboratory averages for $\log_e$ transformed ammonia nitrogen data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

The ordered laboratory averages for the ammonia nitrogen data plotted against the quantiles from a normal distribution are shown in Figure 7.41 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.42 . The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.62

TABLE 7.62. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

	Leachate Sample										Average	Std. dev.
Data	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	86	88	81	87	84	43	87	86	84	78	80	13
Transformed	52	46	51	53	42	83	55	70	70	77	60	14

For the original data it appears that the distribution of the laboratory averages has a heavier lower tail and a heavier upper tail than the lower and upper tails of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e.,closer to a straight line). The lower R^2 values for 9 of the 10 leachate samples and the lower average R^2 for the $\log_e$ transformed data than were obtained for the original data appears to be caused by outlying averages. Several outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed ammonia nitrogen data and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 11 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.63. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.64.

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.65. The hupothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.66.

TABLE 7.63. ANALYSIS OF VARIANCE FOR LOG_e AMMONIA NITROGEN DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	329	936.672	--	--
Leachate Samples	9	495.0672	--	--
Laboratories	10	309.4011	30.9401	21.5*
Lab x Sample	90	129.5398	1.4393	119 *
Residual	220	2.6639	.0121	--

* $P < .005$

TABLE 7.64. VARIANCE COMPONENT ESTIMATES FOR LOG_e AMMONIA NITROGEN DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.4712	(.8604, 3.0721)	σ_R	1.2129	(.9276, 1.7527)
σ^2_{LPLS}	1.4591	(.8501, 3.0686)	σ_{LPLS}	1.2079	(.9220, 1.7517)
σ^2_L	.9834	(.4664, 3.2545)	σ_L	.9916	(.6829, 1.8040)
σ^2_{LS}	.4757	(.3616, .6542)	σ_{LS}	.6897	(.6014, .8088)
σ^2_W	.0121	(.0101, .0147)	σ_W	.1100	(.1006, .1213)

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .27$, $\sigma_L = .16$, and $\sigma = .22$. These values are considerably smaller than the corresponding estimates given in Table 7.66, which indicates that greater precision may be attainable.

TABLE 7.65. ANALYSIS OF VARIANCE FOR LOG_e AMMONIA NITROGEN DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	249	556.608	--	--
Leachate Samples	9	366.731	--	--
Laboratories	24	132.012	5.500	20.5*
Residual	216	57.865	.268	--

* $P < .005$

TABLE 7.66. VARIANCE COMPONENT ESTIMATES FOR LOG_e AMMONIA NITROGEN DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.7912	(.5514, 1.2313)	σ_R	.8895	(.7425, 1.1096)
σ^2_L	.5232	(.3119, 1.0543)	σ_L	.7233	(.5585, 1.0268)
σ^2*	.2680	(.2239, .3267)	σ**	.5177	(.4731, .5716)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Data were received from 23 of the 44 laboratories that agreed to perform the sulfate analysis. The analysis was performed in triplicate by 6 laboratories and in duplicate by 3 laboratories for all 10 leachate samples. A single value or an average value was reported by 8 laboratories. The remaining 6 laboratories reported an unequal number of replicates.

Forty-one values ranging from .5 to 5 mg/ℓ were reported as detection limits (i.e., < value) by 6 laboratories. The difference in magnitude for these values is comparatively large. A complete listing is given in Table A-3 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Twenty-seven 0 mg/ℓ concentration levels were reported for leachate samples A, D, E. F, G, H, I, and J with frequency 1, 5, 1, 2, 5, 8, 1, and 4, respectively. Nine laboratories reported one or more zero concentration levels.

A summary of the analytical results for the 10 leachate samples is given in Table 7.67. The average sulfate concentration of the samples ranged from 4.94 to 2511 mg/ℓ, with the highest value generally 100 times larger than the lowest value for any particular leachate sample.

TABLE 7.67. SUMMARY OF ANALYTICAL RESULTS FOR SULFATE DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	2511	0	4243	2881	413	1032
B	118	2	700	38.5	33.9	189
C	1140	370	1579	1203	93.3	296
D	36.4	0	170	20	2.22	42.5
E	112	0	342	110	5.38	80.5
F	29.5	2.5	141	12.8	3.09	38.0
G	11.5	0	67	4.37	.947	16.1
H	14.6	0	100	3.5	5.48	24.9
I	12.5	0	36	6.83	2.32	11.4
J	4.94	0	13	3.93	2.56	3.97

* All entries in mg/ℓ.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.43. A regression equation was calculated to be $\sigma = .147\ \mu - 4.6$ with an R^2 value of 95%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .815 \log \mu - .459$ with an R^2 value of 86%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.54, 1.09), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

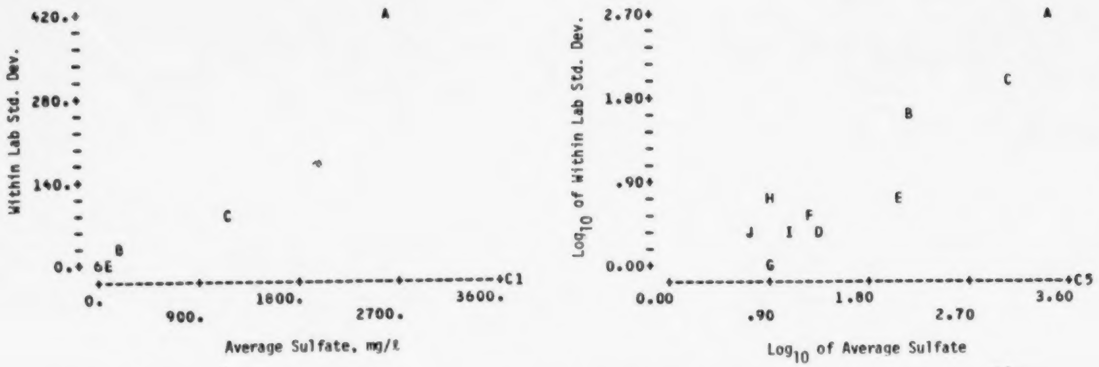

Figure 7.43. Relationship of the within laboratory standard deviation to the sulfate concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.44. A regression equation was calculated to be $\sigma = .376\ \mu + 23.3$ with an R^2 value of 95%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .786 \log \mu + .327$ with an R^2 value of 94%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.62, .95), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, .05 was added to all zero values. These transformed data were used in the statistical analysis of this parameter.

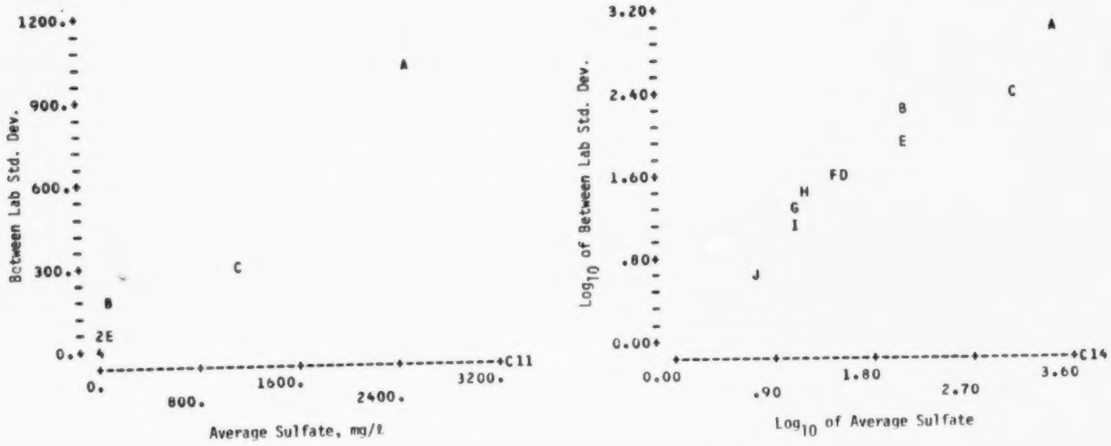

Figure 7.44. Relationship of the between laboratory standard deviation to the sulfate concentration level.

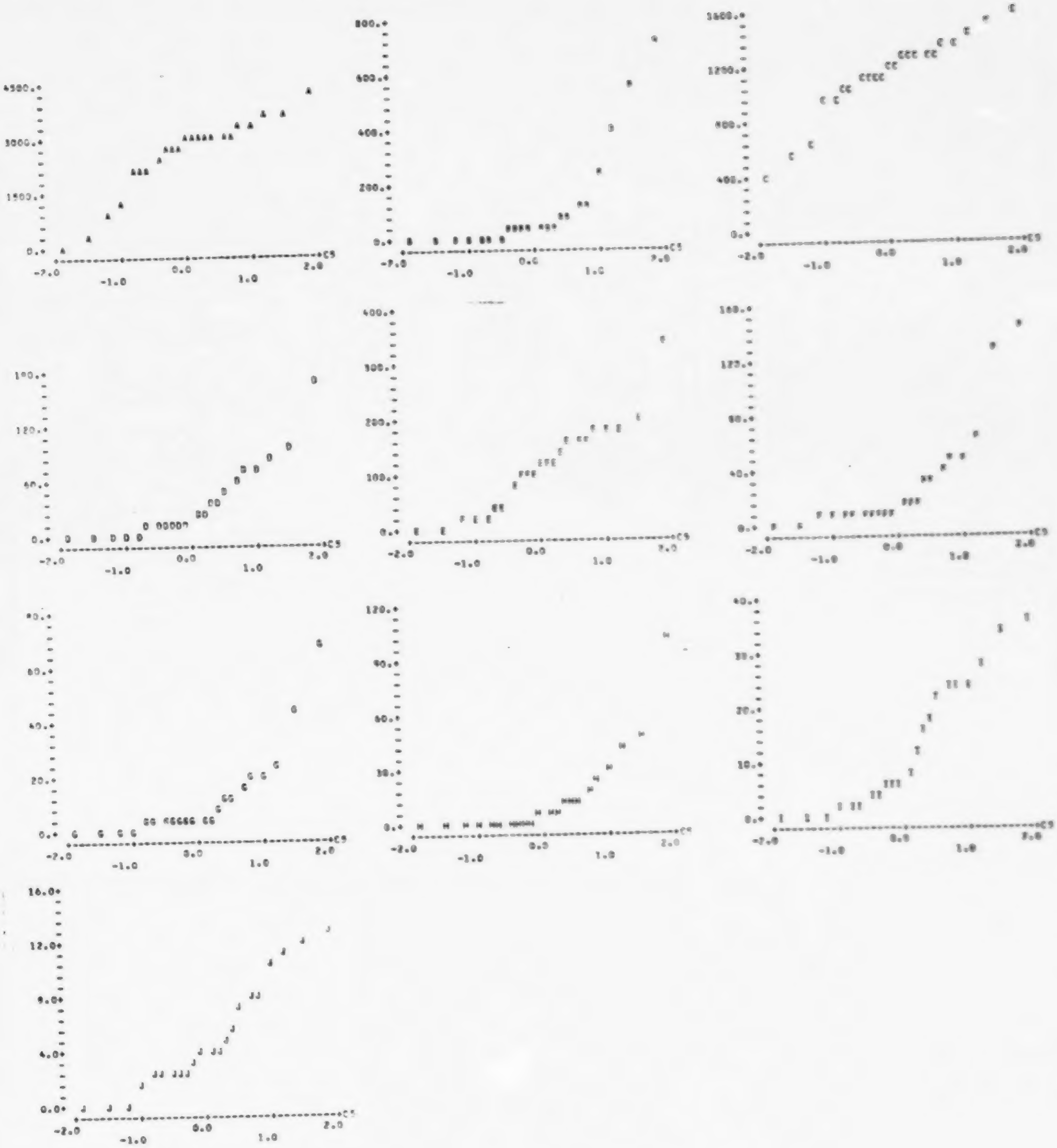

Figure 7.45 . Ordered laboratory averages for sulfate data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

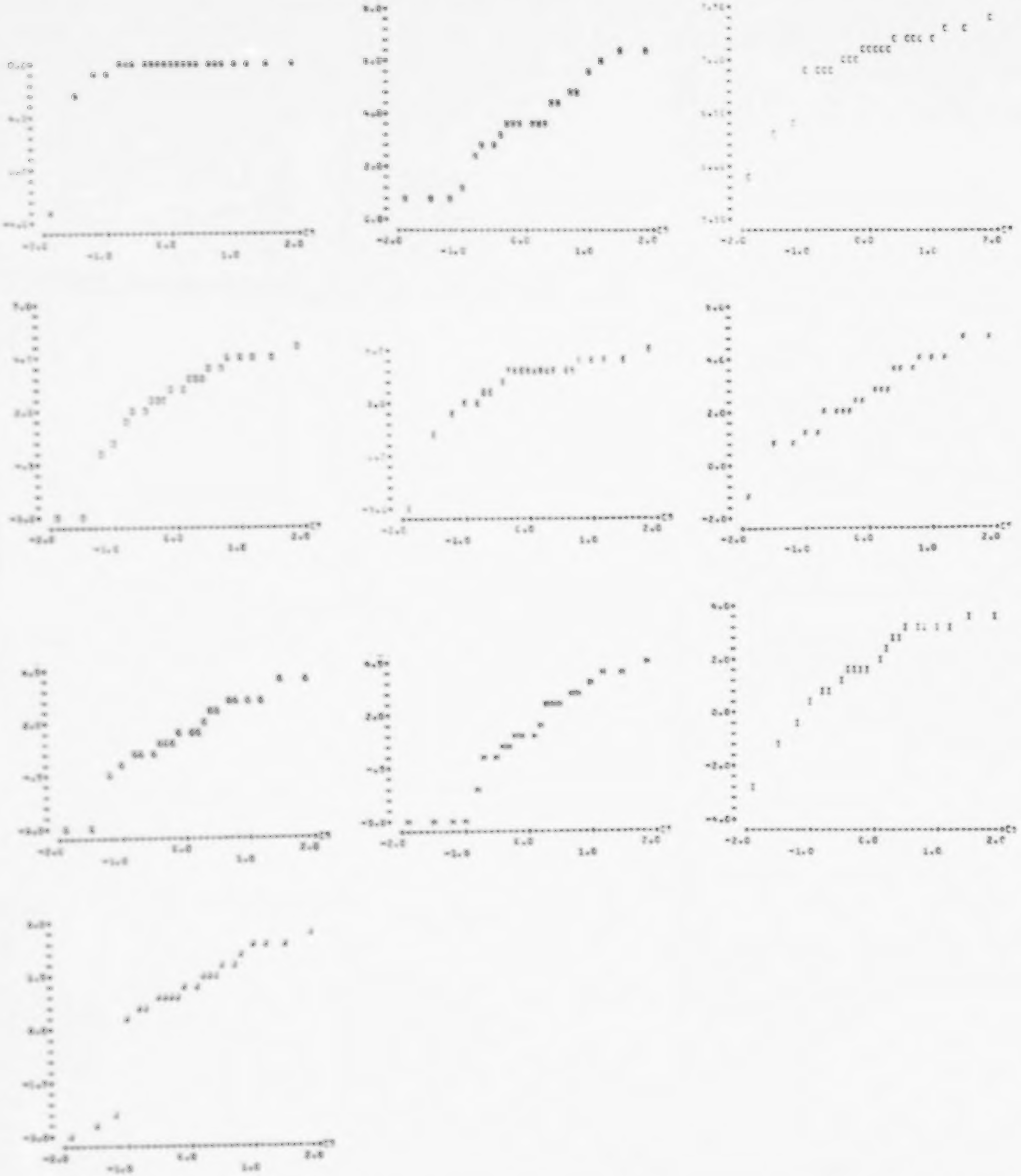

Figure 7.46. Ordered laboratory averages for $\log_e$ transformed sulfate data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

The ordered laboratory averages for the sulfate data plotted against the quantiles from a normal distribution are shown in Figure 7.45 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.46. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.68.

TABLE 7.68. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average R^2	Std. dev. of R^2
	A	B	C	D	E	F	G	H	I	J		
Original	88	63	91	79	92	70	67	64	90	92	80	12
Transformed	36	96	77	86	66	96	91	93	88	80	81	18

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e. closer to a straight line). This observation is supported by the higher R^2 values for 5 of the 10 leachate samples and the slightly higher average R^2 for the $\log_e$ transformed data than were obtained for the original data. For the $\log_e$ transformed data, the low R^2 values in several of the leachate samples appear to be due to the choice of the amount added to zero values before transforming. Outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed sulfate data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 6 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7. 69. The hypothesis that the between laboratory variance component is zero is not rejected. The hypothesis that the laboratory sample interaction variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.70.

TABLE 7.69. ANALYSIS OF VARIANCE FOR LOG_e SULFATE DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	179	1696.623	--	--
Leachate Samples	9	1243.968	--	--
Laboratories	5	62.211	12.442	1.76*
Lab x Sample	45	318.588	7.080	11.8**
Residual	120	71.855	.599	--

* $.1 < p < .25$
** $P < .005$

TABLE 7.70. VARIANCE COMPONENT ESTIMATES FOR LOG_e SULFATE DATA BASED ON LABORATORIES REPORTING THREE REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	2.9381	(2.1320, 4.3094)	σ_R	1.7141	(1.4601, 2.0759)
σ^2_{LPLS}	2.3391	(1.5803, 3.8170)	σ_{LPLS}	1.5294	(1.2571, 1.9537)
σ^2_L	.1787	(.0338393, .4983)	σ_L	.4228	(.1840, 19.8368)
σ^2_{LS}	2.1603	(1.4397, 3.5999)	σ_{LS}	1.4698	(1.1999, 1.8973)
σ^2_W	.5990	(.4722, .7850)	σ_W	.7740	(.6872, .8860)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.71. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.72.

TABLE 7.71. ANALYSIS OF VARIANCE FOR LOG_e SULFATE DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	229	1829.33	--	--
Leachate Samples	9	1117.73	124.19	--
Laboratories	22	143.02	6.50	2.27*
Residual	198	568.57	2.87	--

* $P < .005$

TABLE 7.72. VARIANCE COMPONENT ESTIMATES FOR LOG_e SULFATE DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	3.2330	(2.6794, 3.9789)	σ_R	1.7981	(1.6269, 1.9947)
σ^2_L	.3630	(.1565, 1.5674)	σ_L	.6025	(.3956, 1.2520)
σ^2*	2.8700	(2.3790, 3.5313)	σ**	1.6941	(1.5424, 1.8792)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = 1.1$, $\sigma_L = .66$, and $\sigma = .90$. These values are smaller than the corresponding estimates given in Table 7.72, which indicates that greater precision may be attainable.

Total Phosphorus Data Base

Data were received from 23 of the 43 laboratories that agreed to perform the total phosphorus analysis. The analysis was performed in triplicate by 7 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 8 laboratories. The remaining 7 laboratories reported an unequal number of replicates.

Five values ranging from .03 to 1 mg/ℓ were reported as detection limits (i.e. < value) by 2 laboratories. The difference in magnitude for these values is comparatively large. A complete listing of these values is given in Table A-4 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Twelve 0 mg/ℓ concentration levels were reported for leachate samples H and J with frequency 3 and 9, respectively. Five laboratories reported one or more zero concentration levels.

A summary of the analytical results for the 10 leachate samples is given in Table 7.73. The average total phosphorus concentration of the samples ranged from .252 to 29.4 mg/ℓ, with the highest value generally 300 times larger than the lowest value for any particular leachate sample.

TABLE 7.73. SUMMARY OF ANALYTICAL RESULTS FOR TOTAL PHOSPHORUS DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	29.4	1.18	213	13.5	3.52	53.2
B	12.6	.195	97.5	2.27	1.61	26
C	17.1	.533	119	8.58	.824	27.1
D	2.2	.04	17.5	.493	.549	4.39
E	6.42	.24	60.2	2.58	1.77	12.9
F	6.83	.23	81.2	2.2	.589	17
G	4.17	.1	25.7	1.95	1.98	5.96
H	2.49	0.0	13.5	1.62	.227	3.2
I	2.94	.06	46.5	1.58	.221	9.67
J	.252	0.0	2.1	.04	.528	.555

* All entries in mg/ℓ.

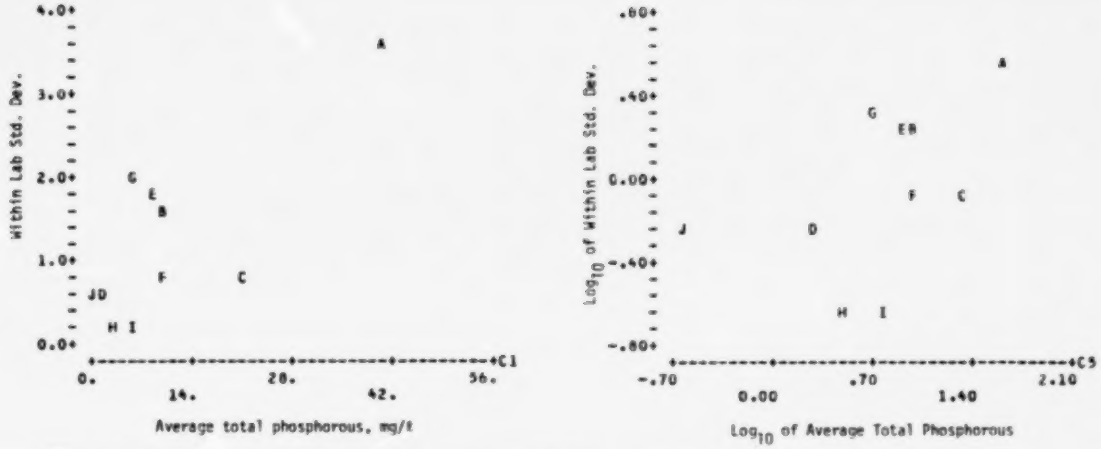

Figure 7.47. Relationship of the within laboratory standard deviation to the total phosphorus concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.48. A regression equation was calculated to be $\sigma = 1.76\ \mu + .93$ with an R^2 value of 98%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .977 \log \mu + .292$ with an R^2 value of 97%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.84, 1.11), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

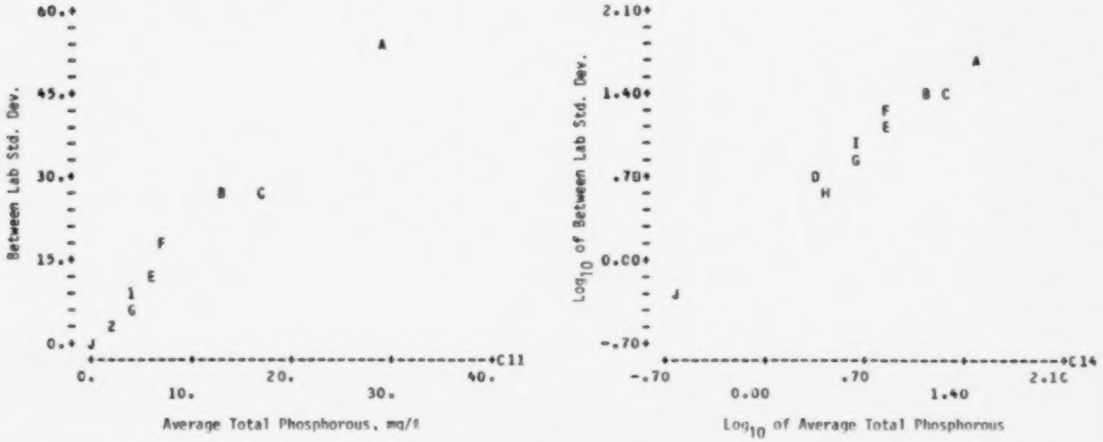

Figure 7.48. Relationship of the between laboratory standard deviation to the total phosphorus concentration level.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.47. A regression equation was calculated to be $\sigma = .0639\ \mu + .542$ with an R^2 value of 57%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .339 \log \mu - .320$ with an R^2 value of 27%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (-.12, .80), which suggests that a square root transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the between laboratory variance. Before applying the transformation, .0025 was added to all zero values. Although the square root transformation was indicated to stabilize the within laboratory variance, the appearance of the graphs and low R^2 value makes the choice of a transformation uncertain. The logarithmic transformed data were used in the statistical analysis of this parameter.

The ordered laboratory averages for the total phosphorus data plotted against the quantiles from a normal distribution are shown in Figure 7.49 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.50. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.74.

TABLE 7.74. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

	Leachate Sample										Average	Std. dev.
Data	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	45	51	53	51	44	34	62	64	33	48	49	10
Transformed	86	95	92	96	94	92	95	80	88	97	92	5

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for all 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in some of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

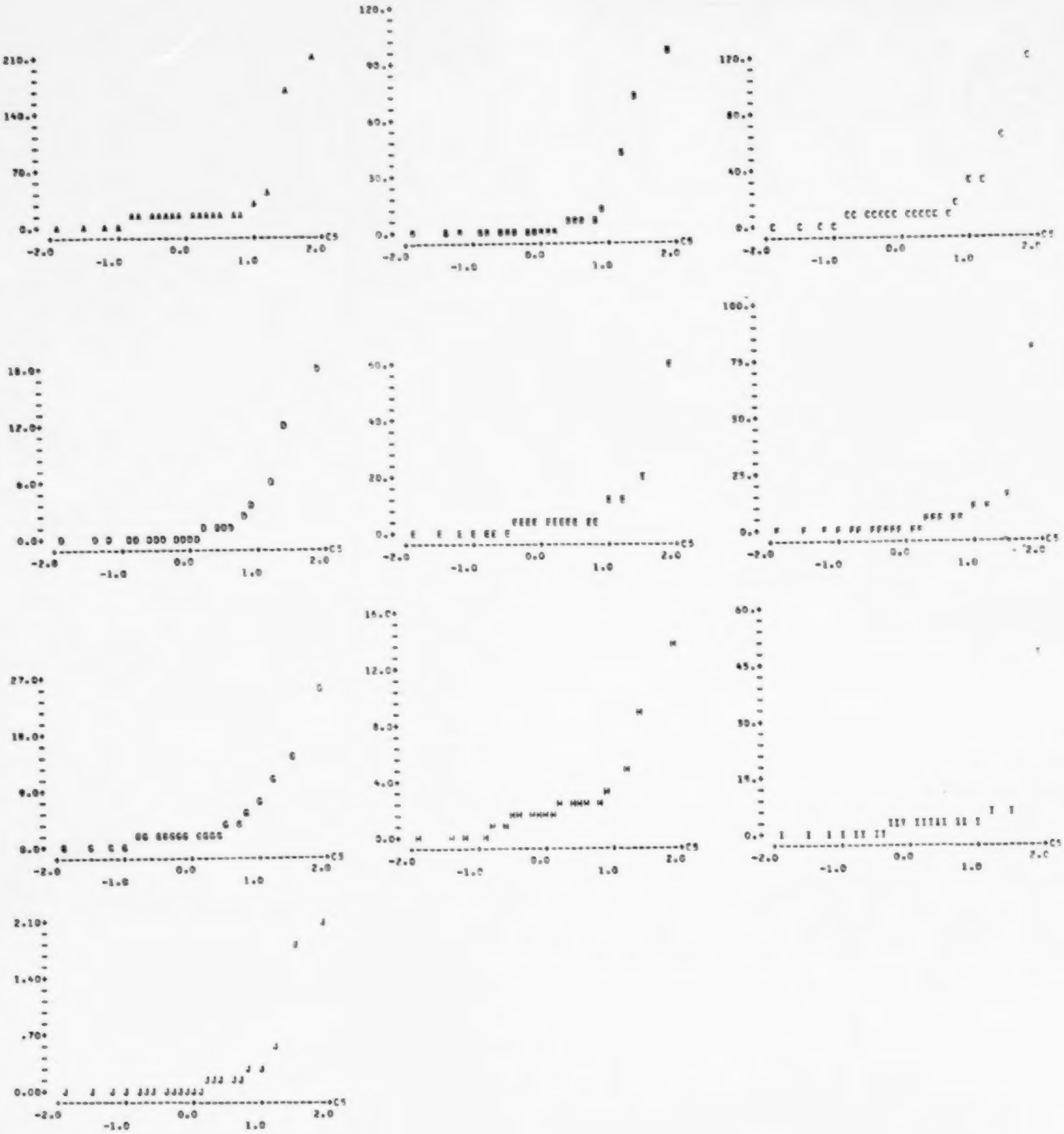

Figure 7.49. Ordered laboratory averages for total phosphorus data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

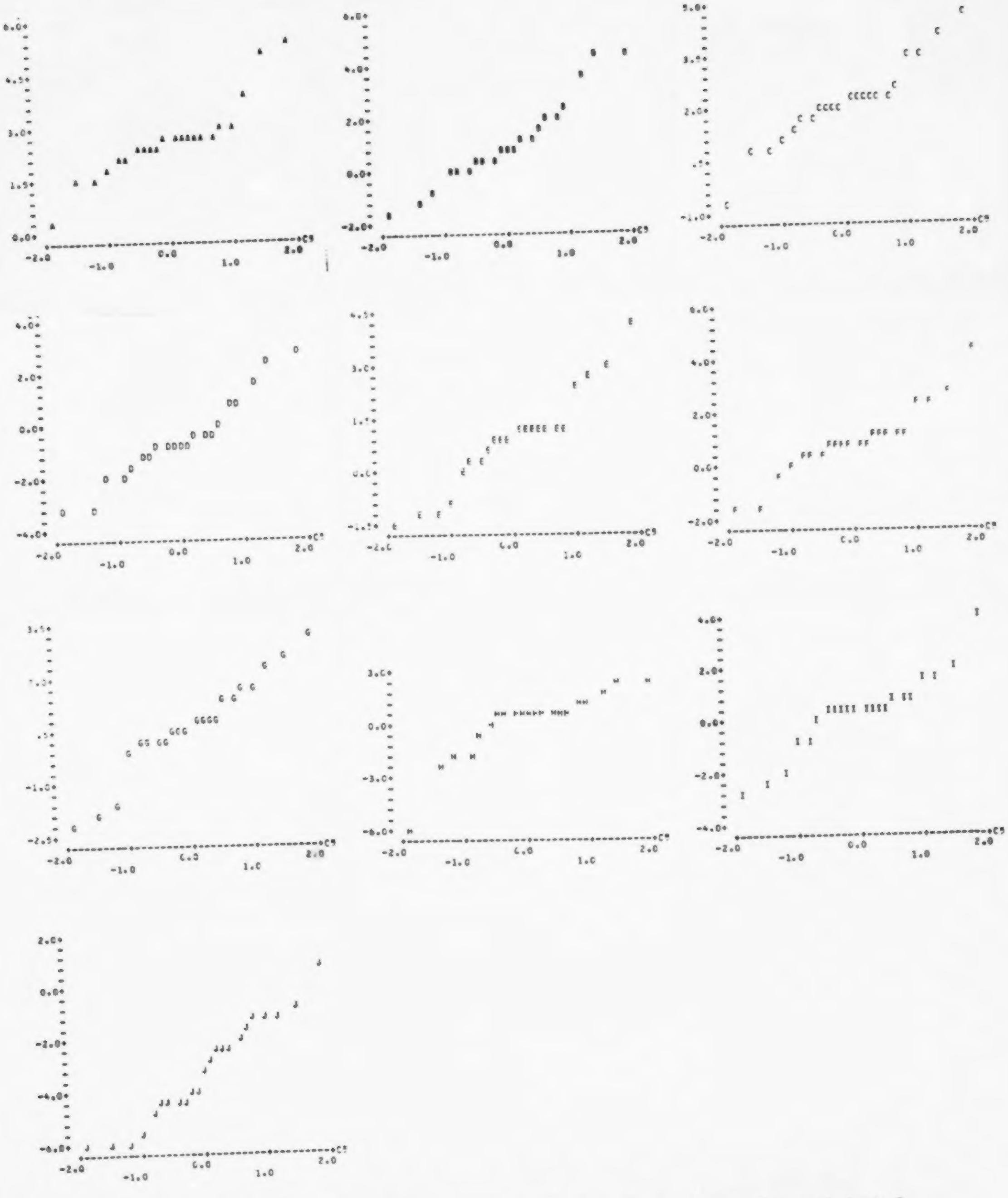

Figure 7.50. Ordered laboratory averages for $\log_e$ transformed total phosphorus data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed total phosphorus data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 7 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.75. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.76.

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.77. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.78.

TABLE 7.75. ANALYSIS OF VARIANCE FOR LOG_e TOTAL PHOSPHORUS DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	209	863.232	--	--
Leachate Samples	9	482.832	53.648	--
Laboratories	6	258.538	43.090	30.0*
Lab x Sample	54	77.422	1.434	4.52*
Residual	140	44.440	.317	--

* $P < .005$

TABLE 7.76. VARIANCE COMPONENT ESTIMATES FOR LOG_e TOTAL PHOSPHORUS DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	2.0779	(1.0777, 5.5521)	σ_R	1.4415	(1.0381, 2.3563)
σ^2_{LPLS}	1.7609	(.8307, 5.9101)	σ_{LPLS}	1.3270	(.9114, 2.4311)
σ^2_L	1.3885	(.5630, 7.2699)	σ_L	1.1784	(.7503, 2.6963)
σ^2_{LS}	.3723	(.2409, .6505)	σ_{LS}	.6102	(.4909, .8066)
σ^2_W	.3170	(.2541, .4067)	σ_W	.5630	(.5041, .6377)

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .63$, $\sigma_L = .30$, and $\sigma = .55$. These values are smaller than the corresponding estimates given in Table 7.78, which indicates that greater precision may be attainable.

TABLE 7.77. ANALYSIS OF VARIANCE FOR LOG_e TOTAL PHOSPHORUS DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	229	1001.929	--	--
Leachate Samples	9	539.820	--	--
Laboratories	22	330.034	15.002	22.5*
Residual	198	132.074	.667	--

* $P < .005$

Chloride Data Base

Data were received from 27 of the 49 laboratories that agreed to perform the chloride analysis. The analysis was performed in triplicate by 16 laboratories for all 10 leachate samples. A single value or an average value was reported by 8 laboratories. The remaining 3 laboratories reported an unequal number of replicates.

TABLE 7.78. VARIANCE COMPONENT ESTIMATES FOR LOG_e TOTAL PHOSPHORUS DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	2.1005	(1.4302, 3.3865)	σ_R	1.4493	(1.1959, 1.8402)
σ^2_L	1.4335	(.8396, 2.9851)	σ_L	1.1973	(.9163, 1.7278)
σ^2*	.6670	(.5529, .8207)	σ**	.8167	(.7436, .9059)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

A summary of the analytical results for the 10 leachate samples is given in Table 7.79 . The average chloride concentration of the samples ranged from 37.5 to 24,050 mg/ℓ, with the highest value generally 200 times larger than the lowest value for any particular leachate sample .

TABLE 7.79. SUMMARY OF ANALYTICAL RESULTS FOR CHLORIDE DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	24050	15	36097	25133	1315	5951
B	505	15	1022	465	33.6	180
C	2113	15	7717	1810	73.5	1302
D	1445	539	2700	1300	65.1	458
E	275	174	910	217	13.9	162
F	107	3.1	351	77.5	20.1	73.2
G	170	5.1	465	165	27.5	83.5
H	37.5	0.5	160	25.6	4.08	39.4
I	552	3	966	550	35.2	194
J	85.6	7.7	138	82.3	5.64	23.4

* All entries in mg/ℓ.

Thirteen values ranging from 1 to 30 mg/ℓ were reported as detection limits (i.e., < value). The difference in magnitude for these values is comparatively large. A complete listing of these values is given in Table A-5 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. No 0 mg/ℓ concentration levels were reported.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.51. A regression equation was calculated to be σ .0555 μ - 2.30 with an R^2 value of 100%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .837 \log \mu - .724$ with an R^2 value of 93%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.65, 1.03), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

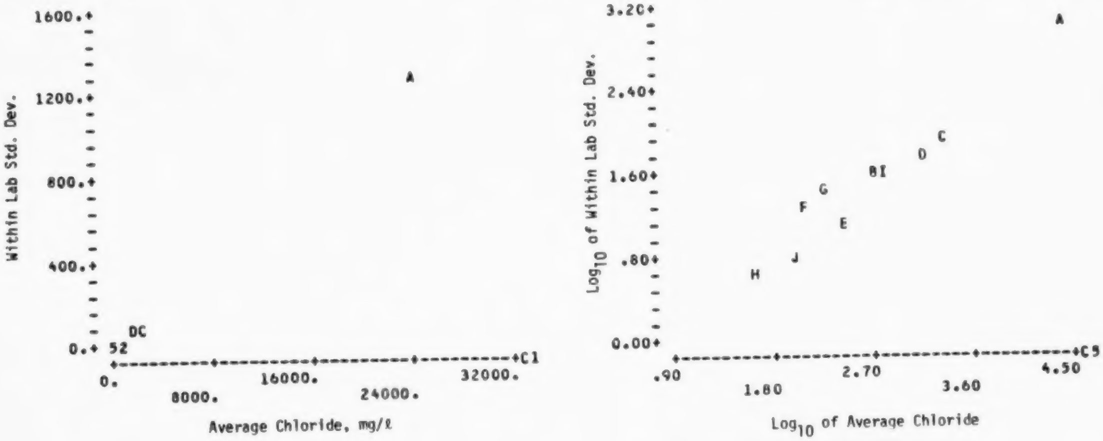

Figure 7.51. Relationship of the within laboratory standard deviation to the chloride concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.52. A regression equation was calculated to be $\sigma = .244 \mu + 130$ with an R^2 value of 98%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .859 \log \mu + .028$ with an R^2 value of 95%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.69, 1.02), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

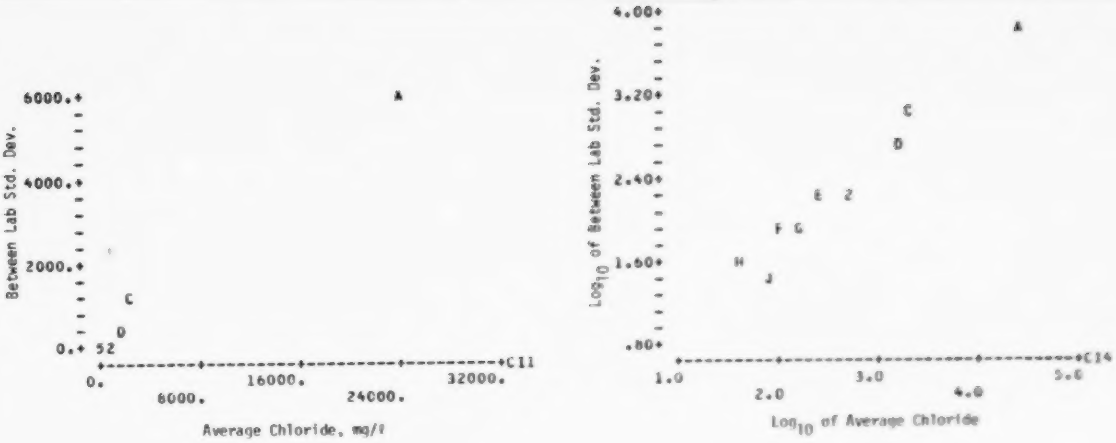

Figure 7.52. Relationship of the between laboratory standard deviation to the chloride concentration level.

The natural logarithms (base e) of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. These transformed data were used in the statistical analysis of this parameter.

The ordered laboratory averages for the chloride data plotted against the quantiles from a normal distribution are shown in Figure 7.53 for the ten leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.54 . The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.80.

TABLE 7.80 . R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average R^2	Std. dev. of R^2
	A	B	C	D	E	F	G	H	I	J		
Original	66	74	47	70	51	74	72	58	70	74	66	10
Transformed	24	42	37	73	65	69	57	70	37	45	52	17

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). The lower R^2 values for 7 of the 10 leachate samples, the lower average R^2 , and greater standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data appear to be caused by outlying averages. Outlying averages are present in most of the leachate samples however, which appear to be responsible for the low R^2 values for both the original and transformed data.

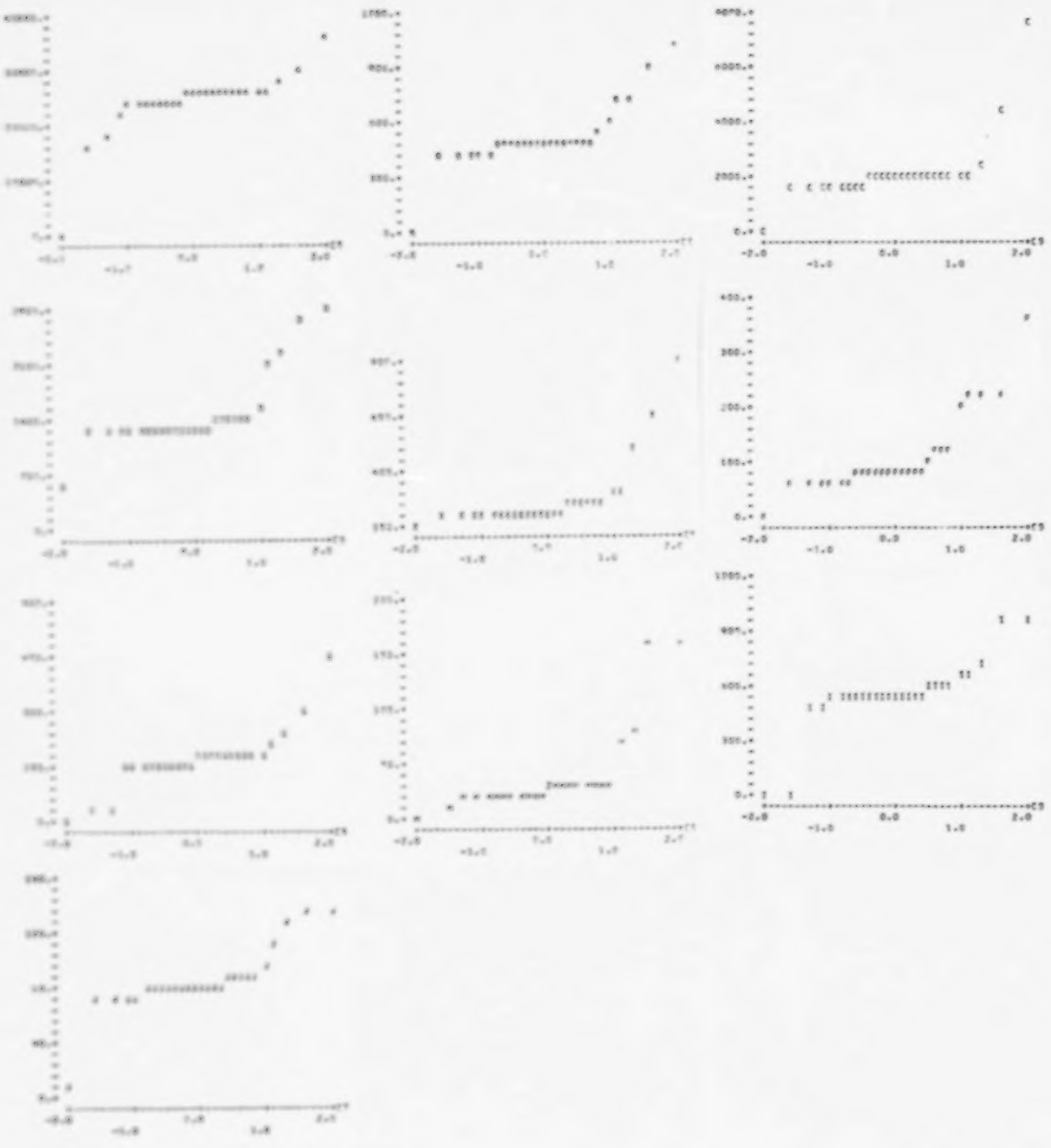

Figure 7.53. Ordered laboratory averages for chloride data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

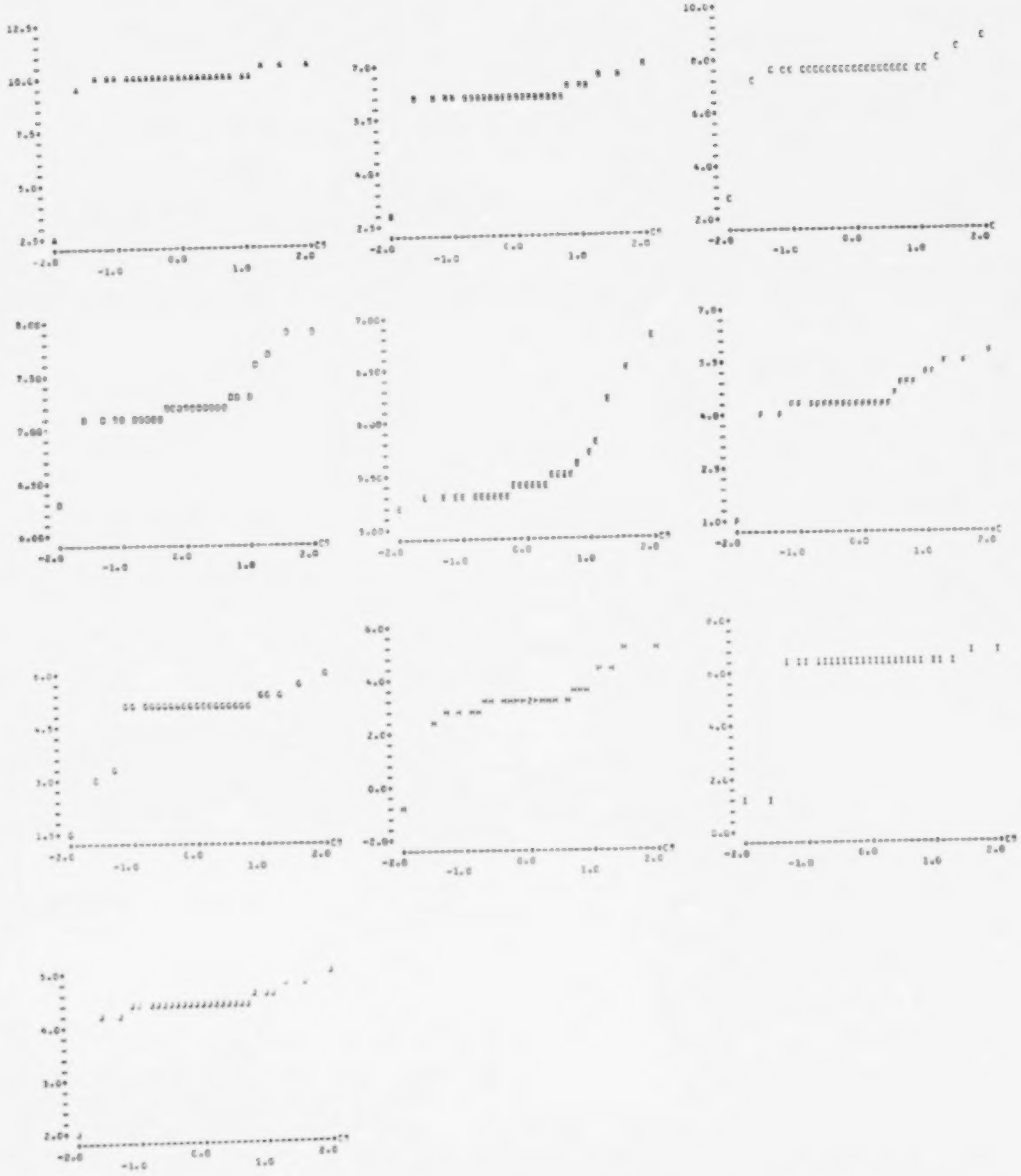

Figure 7.54. Ordered laboratory averages for $\log_e$ transformed chloride data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed chloride data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 16 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.81. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.82.

TABLE 7.81. ANALYSIS OF VARIANCE FOR LOG_e CHLORIDE DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	479	1796.8162	--	--
Leachate Samples	9	1372.1527	--	--
Laboratories	15	164.0003	10.9334	5.68*
Lab x Sample	135	259.7131	1.9238	641 *
Residual	320	.9501	.0030	--

* $P < .005$

TABLE 7.82. VARIANCE COMPONENT ESTIMATES FOR LOG_e CHLORIDE DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.9436	(.7063, 1.3252)	σ_R	.9714	(.8404, 1.1512)
σ^2_{LPLS}	.9406	(.7035, 1.3224)	σ_{LPLS}	.9698	(.8387, 1.1500)
σ^2_L	.3003	(.1472, .9160)	σ_L	.5480	(.3837, .9571)
σ^2_{LS}	.6403	(.5111, .8257)	σ_{LS}	.8002	(.7149, .9087)
σ^2_W	.0030	(.0026, .0035)	σ_W	.0548	(.0508, .0594)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.83. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.84.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .17$, $\sigma_L = .032$, and $\sigma = .16$. These values are considerably smaller than the corresponding estimates given in Table 7.84, which indicates that greater precision may be attainable.

TABLE 7.83. ANALYSIS OF VARIANCE FOR LOG_e CHLORIDE DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	269	1096.158	--	--
Leachate Samples	9	874.554	--	--
Laboratories	26	79.235	3.047	5.01*
Residual	234	142.370	.008	--

* $P < .005$

TABLE 7.84. VARIANCE COMPONENT ESTIMATES FOR LOG_e CHLORIDE DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.8519	(.6876, 1.0835)	σ_R	.9230	(.8292, 1.0409)
σ^2_L	.2439	(.1364, .5551)	σ_L	.4939	(.3694, .7451)
σ^2*	.6080	(.5113, .7352)	σ**	.7797	(.7150, .8574)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Alkalinity Data Base

Data were received from 25 of the 45 laboratories that agreed to perform the alkalinity analysis. The analysis was performed in triplicate by 13 laboratories for all 10 leachate samples. A single value or an average value was reported by 6 laboratories. The remaining 6 laboratories reported an unequal number of replicates. One laboratory used two methods in the determination of this parameter.

No values were reported as detection limits (i.e., < value) for this parameter, and no 0 mg/ℓ concentration levels were reported.

TABLE 7.85. SUMMARY OF ANALYTICAL RESULTS FOR ALKALINITY DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	7400	2480	10733	7883	125	2279
B	3687	2100	17900	2993	58.4	3070
C	6260	3460	9303	6147	106	1492
D	3553	1687	5080	3708	100	1037
E	1963	274	3203	1960	58.8	530
F	1701	113	3870	1600	55.4	715
G	2126	1400	5733	1967	93.6	845
H	884	364	2392	853	48.8	391
I	2716	2160	6133	2433	69.1	981
J	432	342	993	363	49.8	177

*All entries in mg/ℓ

A summary of the analytical results for the 10 leachate samples is given in Table 7.85 . The average alkalinity concentration of the samples ranged from 432 to 7400 mg/ℓ, with the highest value generally 5 times larger than the lowest value for any particular leachate sample.

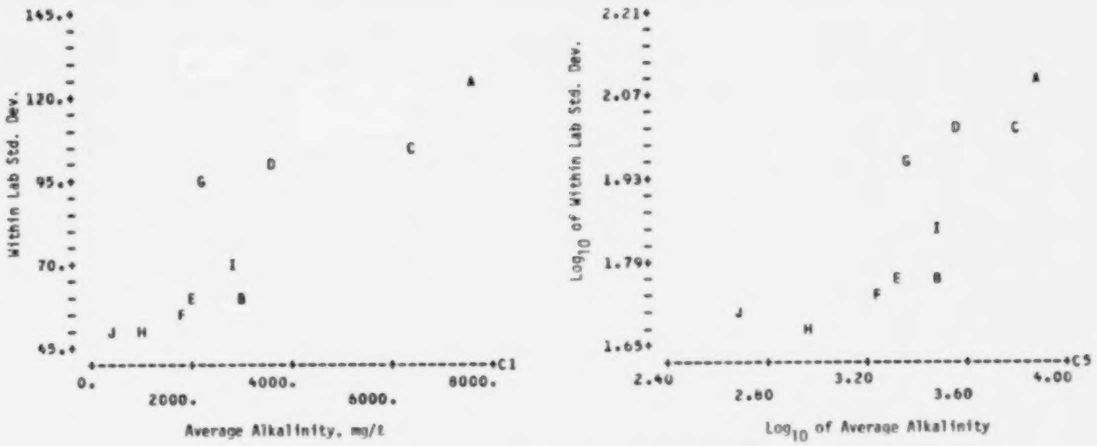

Figure 7.55. Relationship of the within laboratory standard deviation to the alkalinity concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.56. A regression equation was calculated to be $\sigma = .286\ \mu + 274$ with an R^2 value of 51%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .892 \log \mu - .064$ with an R^2 value of 84%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.57, 1.21), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

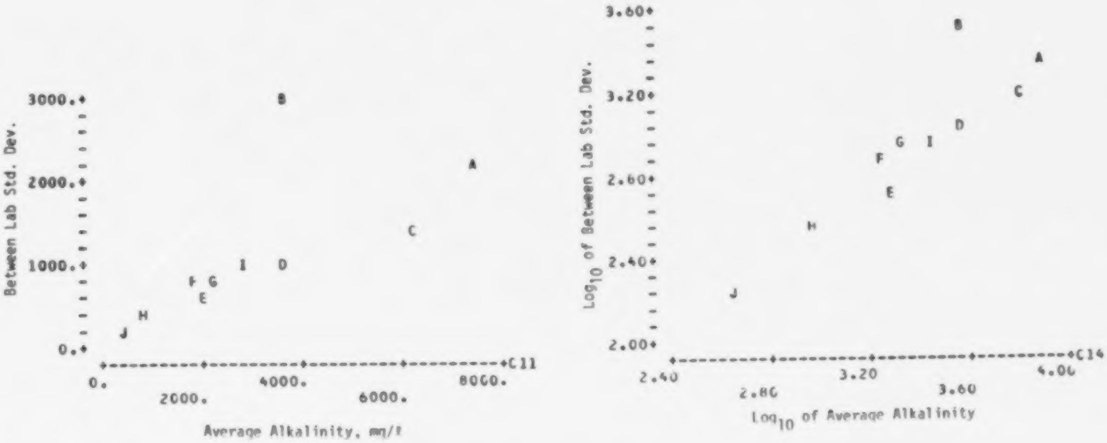

Figure 7.56. Relationship of the between laboratory standard deviation to the alkalinity concentration level.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.55. A regression equation was calculated to be $\sigma = .0105\ \mu + 43.8$ with an R^2 value of 78%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .344 \log \mu + .698$ with an R^2 value of 70%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.16, .53), which suggests that a square root transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. These transformed data were used in the statistical analysis of this parameter.

The ordered laboratory averages for the alkalinity data plotted against the quantiles from a normal distribution are shown in Figure 7.57 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.58. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.86.

TABLE 7.86. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average R^2	Std. dev. of R^2
	A	B	C	D	E	F	G	H	I	J		
Original	96	40	98	97	89	81	58	77	47	50	73	23
Transformed	89	71	95	94	59	61	79	95	56	56	76	17

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data, (i.e. closer to a straight line). This observation is supported by the higher R^2 values for 5 of the 10 leachate samples, the slightly greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in some of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

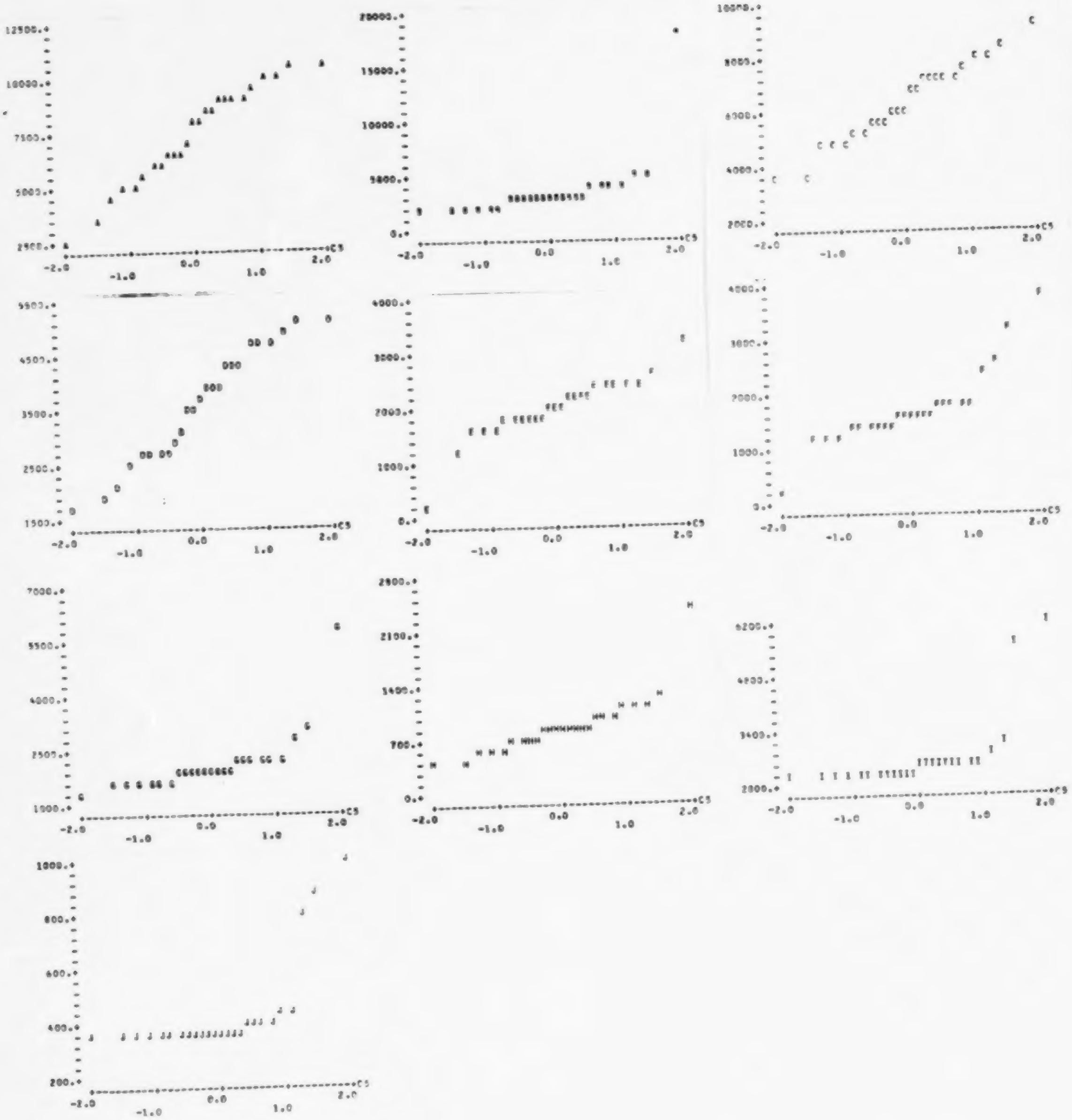

Figure 7.57. Ordered laboratory averages for alkalinity data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

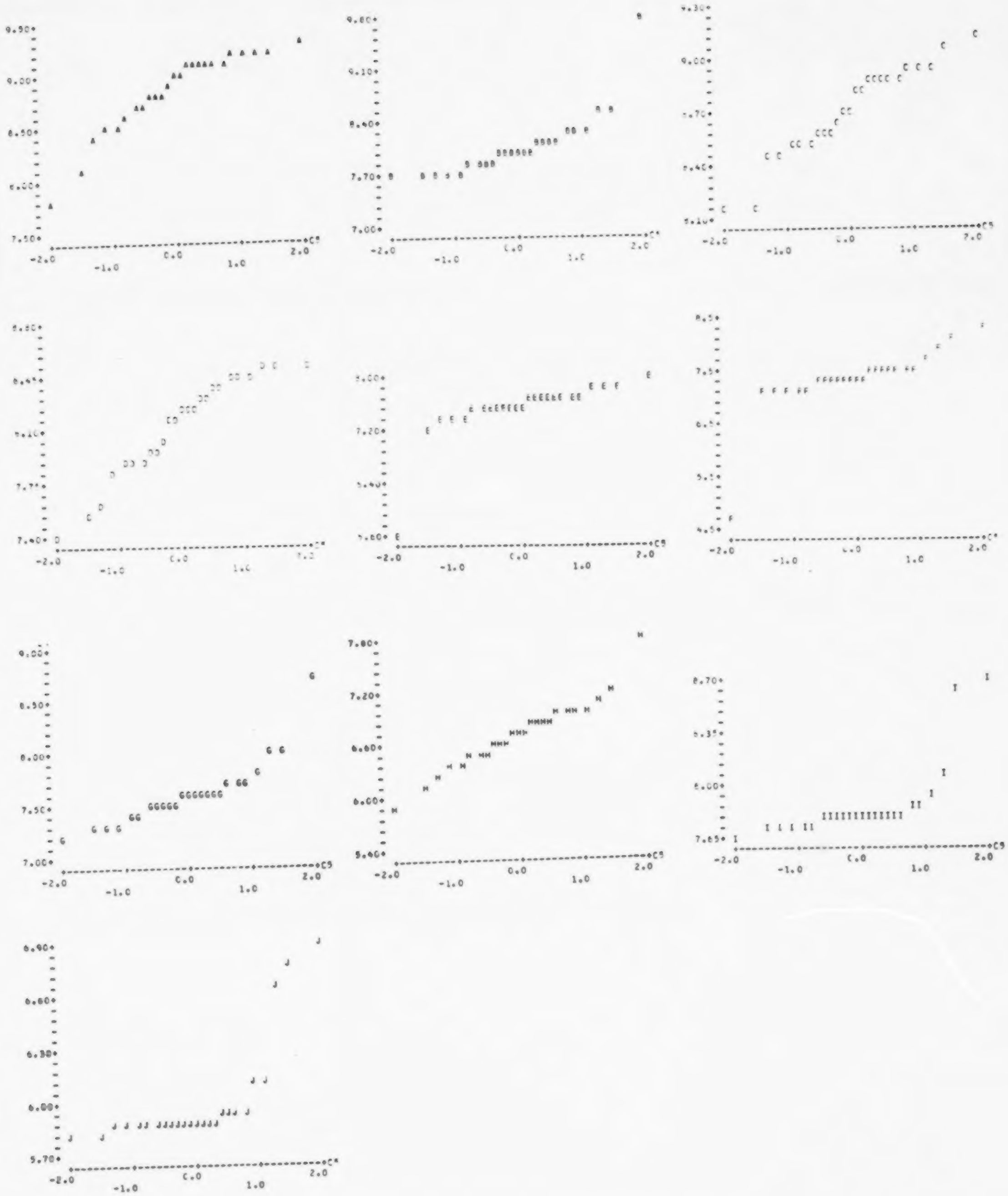

Figure 7.58. Ordered laboratory averages for $\log_e$ transformed alkalinity data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed alkalinity data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

TABLE 7.87. ANALYSIS OF VARIANCE FOR LOG_e ALKALINITY DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	389	329.62851		
Leachate Samples	9	256.87259		
Laboratories	12	30.83323	2.56944	6.66*
Lab x Sample	108	41.64317	.38558	357 *
Residual	260	.27952	.00108	

* P < .005

The data from 13 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.87. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.88.

TABLE 7.88. VARIANCE COMPONENT ESTIMATES FOR LOG_e ALKALINITY DATA BASED ON LABORATORIES REPORTING THREE REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.2020	(.1438, .3049)	σ_R	.4495	(.3792, .5522)
σ^2_{LPLS}	.2010	(.1428, .3038)	σ_{LPLS}	.4483	(.3779, .5512)
σ^2_L	.0728	(.0340, .2506)	σ_L	.2698	(.1844, .5006)
σ^2_{LS}	.1282	(.0998, .1708)	σ_{LS}	.3580	(.3159, .4132)
σ^2_W	.0011	(.0009, .0013)	σ_W	.0329	(.0303, .0360)

TABLE 7.89. ANALYSIS OF VARIANCE FOR LOG_e ALKALINITY DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	249	202.4977	--	--
Leachate Samples	9	167.7867	--	--
Laboratories	24	14.1544	.5898	6.20*
Residual	216	20.5565	.0952	--

* $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.89. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.90.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .19$, $\sigma_L = .12$, and $\sigma = .15$. These values are smaller than the corresponding estimates given in Table 7.90, which indicates that greater precision may be attainable.

TABLE 7.90. VARIANCE COMPONENT ESTIMATES FOR LOG_e ALKALINITY DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.1447	(.1137, .1903)	σ_R	.3803	(.3372, .4362)
σ^2_L	.0495	(.0278, .1118)	σ_L	.2224	(.1667, .3343)
σ^2*	.0952	(.0795, .1161)	σ**	.3085	(.2820, .3407)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Nitrate Nitrogen Data Base

Data were received from 23 of the 45 laboratories that agreed to perform the nitrate analysis. The analysis was performed in triplicate by 13 laboratories for all 10 leachate samples. A single value or an average value was reported by 8 laboratories. The remaining 2 laboratories reported an unequal number of replicates.

One hundred eleven values ranging from .01 to .1 mg/ℓ were reported as detection limits (i.e., < value) by 12 laboratories. The difference in magnitude for these values is comparatively large. A complete listing of these values is given in Table A-6 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Five 0 mg/ℓ concentration levels were reported which occurred in leachate samples E, G, and I with frequency 1, 3, and 1, respectively. Three laboratories reported one or more zero concentration level.

A summary of the analytical results for the 10 leachate samples is given in Table 7.91. The average nitrate concentration of the samples ranged from .344 to 4.98 mg/ℓ, with the highest value generally 2000 times larger than the lowest value for any particular leachate sample.

TABLE 7.91. SUMMARY OF ANALYTICAL RESULTS FOR NITRATE NITROGEN

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	2.88	.01	50.7	.367	.406	10.4
B	.595	.005	9.47	.05	.0602	1.97
C	3.41	.01	66.8	.195	.134	14.2
D	2.07	.01	40	.05	.0185	8.3
E	.526	0.0	6.93	.1	.0235	1.43
F	.608	.005	7.47	.1	.081	1.58
G	.383	0.0	5.08	.05	.0424	1.05
H	.344	.0015	2.33	.067	.0698	.665
I	4.98	0.0	98.6	.06	.53	19.7
J	1.02	.0035	5.83	.767	.778	1.32

*All entries in mg/ℓ.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.59. A regression equation was calculated to be $\sigma = .043\ \mu + .108$ with an R^2 value of 16%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .612 \log \mu - 1.10$ with an R^2 value of 23%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (-.30, 1.53), which suggests that a square root or logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

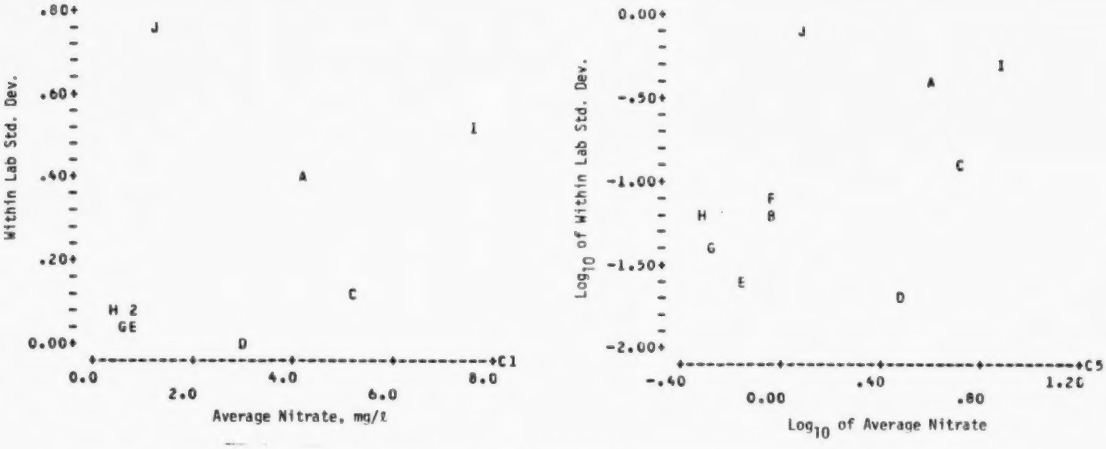

Figure 7.59. Relationship of the within laboratory standard deviation to the nitrate nitrogen concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.60. A regression equation was calculated to be $\sigma = 4.19\ \mu - .989$ with an R^2 value of 99%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.22 \log \mu + .449$ with an R^2 value of 94%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.97, 1.47), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the between laboratory variance. Before applying the transformation, .0015 was added to all zero values. Although the square root or logarithmic transformation was indicated to stabilize the within laboratory variance, the appearance of the graphs and low R^2 value makes the choice of a transformation uncertain. The logarithmic transformed data were used in the statistical analysis of this parameter.

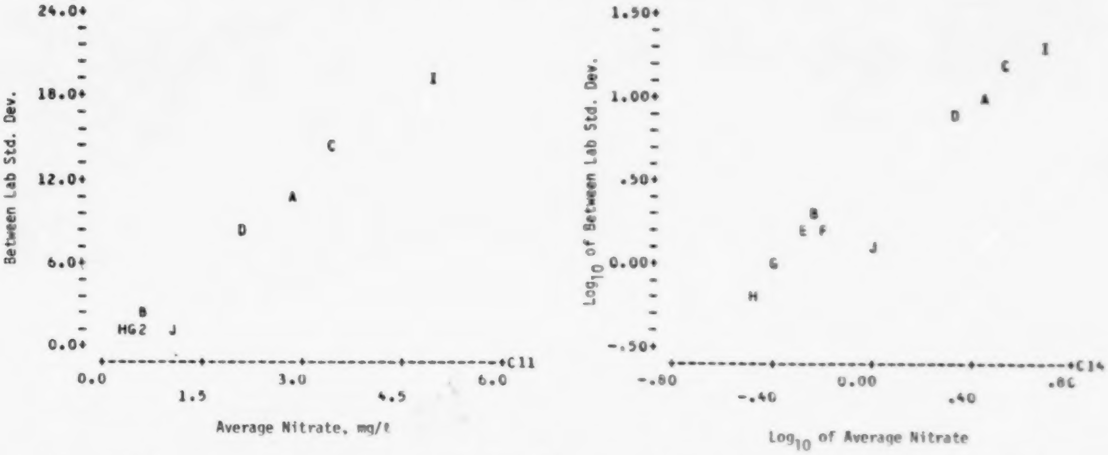

Figure 7.60. Relationship of the between laboratory standard deviation to the nitrate nitrogen concentration level.

The ordered laboratory averages for the nitrate data plotted against the quantiles from a normal distribution are shown in Figure 7.61 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.62. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.92.

TABLE 7.92. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample A	B	C	D	E	F	G	H	I	J	Average R^2	Std. dev. of R^2
Original	24	29	22	24	34	38	35	54	24	72	36	16
Transformed	93	94	91	88	98	98	98	98	93	92	94	4

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data, (i.e. closer to a straight line). This observation is supported by the higher R^2 values for all 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in some of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

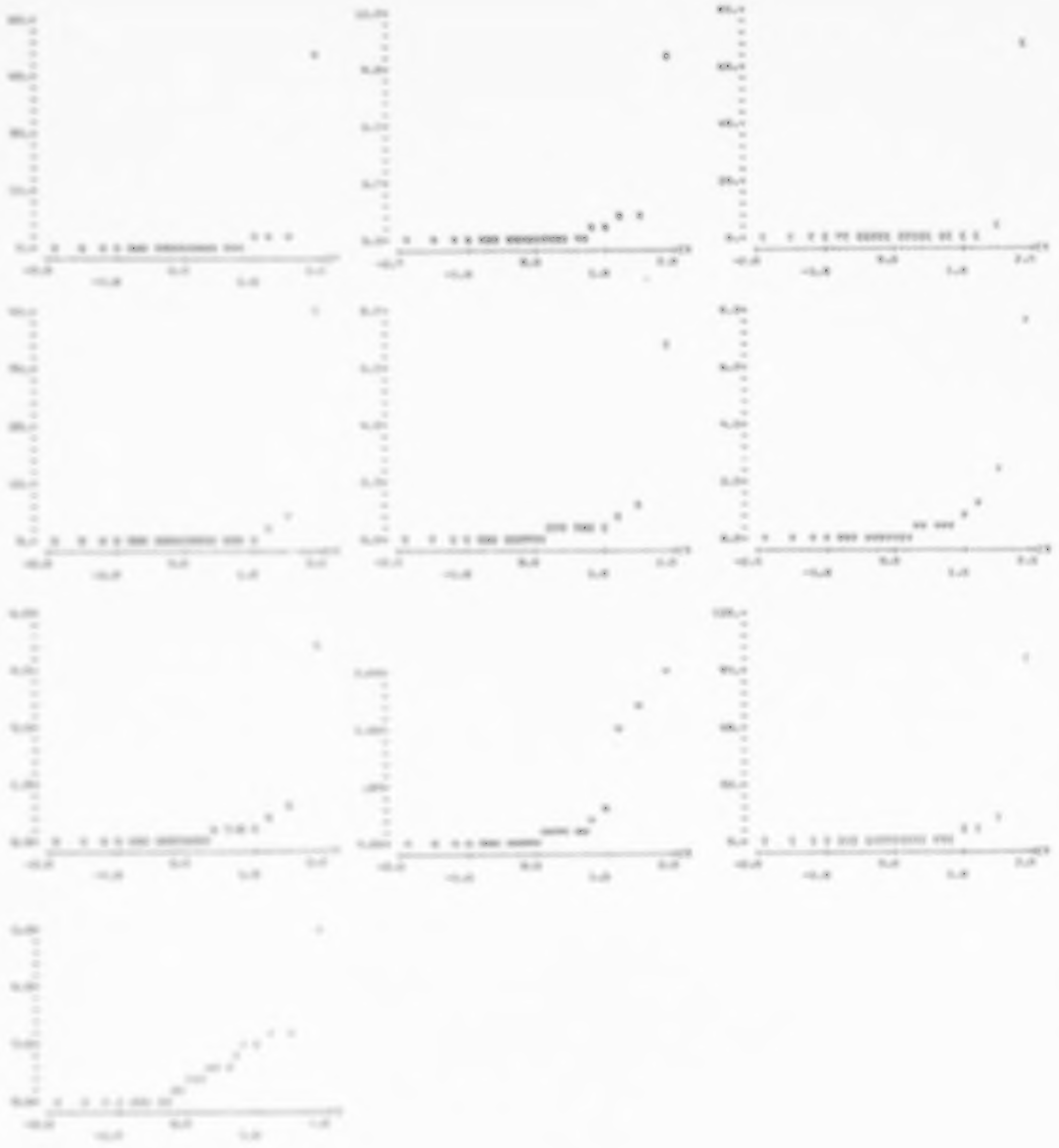

Figure 7.61. Ordered laboratory averages for nitrate nitrogen data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

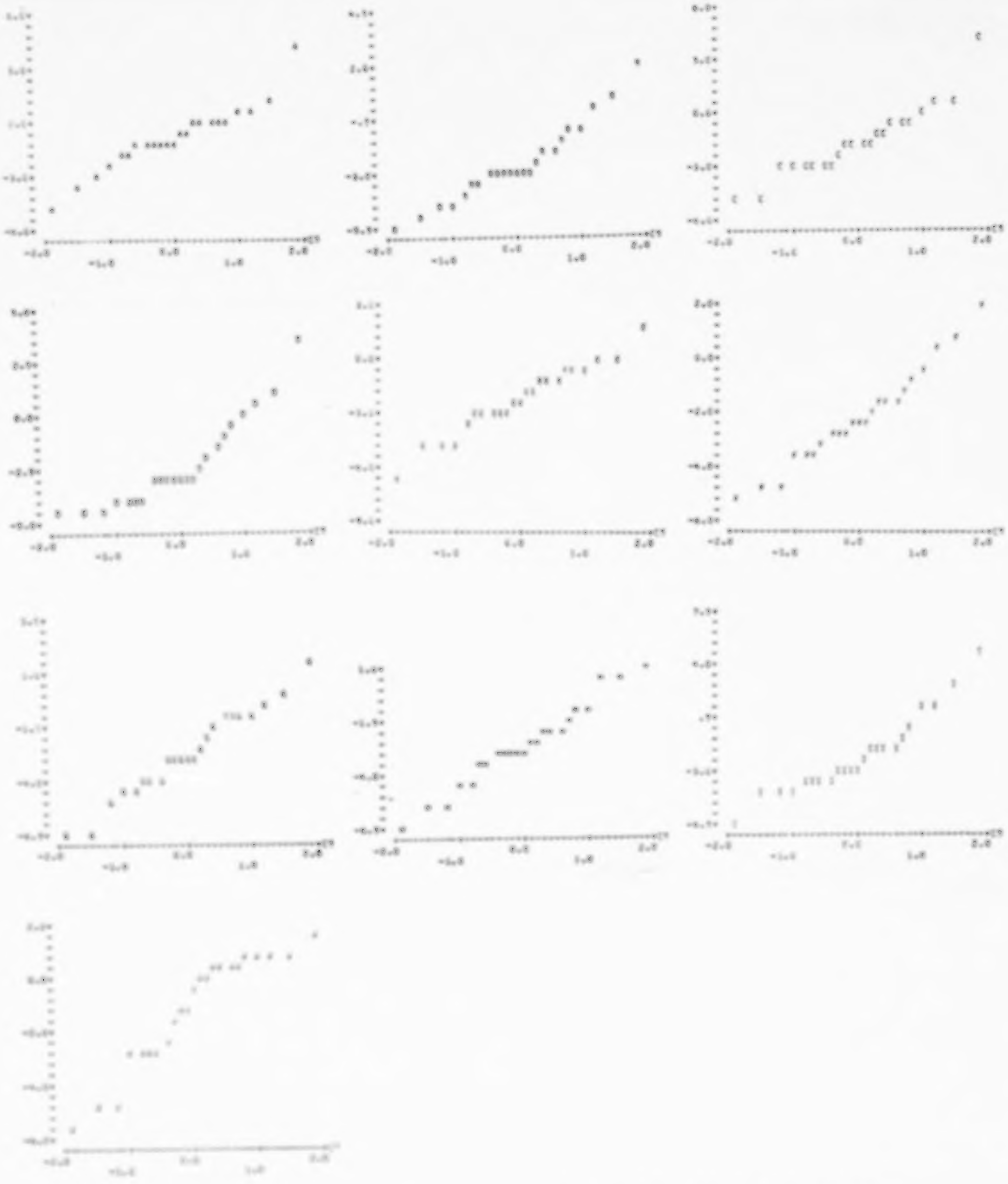

Figure 7.62. Ordered laboratory averages for $\log_e$ transformed nitrate nitrogen data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates given below are for the $\log_e$ transformed nitrate data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 13 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.93. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.94.

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.95. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.96.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = 1.4$, $\sigma_L = .90$, and $\sigma = 1.1$. These values are smaller than the corresponding estimates given in Table 7.96, which indicates that greater precision may be attainable.

TABLE 7.93. ANALYSIS OF VARIANCE FOR LOG_e NITRATE NITROGEN DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	389	1997.8093	--	--
Leachate Samples	9	218.7612	24.3068	--
Laboratories	12	1203.5030	100.2919	19.1*
Lab x Sample	108	565.8659	5.2395	141 *
Residual	260	9.6792	.0372	--

* $P < .005$

TABLE 7.94. VARIANCE COMPONENT ESTIMATES FOR LOG_e NITRATE NITROGEN DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	4.9397	(3.0518, 9.3382)	σ_R	2.2225	(1.7469, 3.0559)
σ^2_{LPLS}	4.9025	(3.0192, 9.3196)	σ_{LPLS}	2.2142	(1.7376, 3.0528)
σ^2_L	3.1684	(1.5800, 9.2643)	σ_L	1.7800	(1.2570, 3,0437)
σ^2_{LS}	1.7341	(1.3485, 2.3136)	σ_{LS}	1.3169	(1.1612, 1.5210)
σ^2_W	.0372	(.0316, .0445)	σ_W	.1929	(.1776, .2110)

TABLE 7.95. ANALYSIS OF VARIANCE FOR LOG_e NITRATE NITROGEN DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	229	949.01		
Leachate Samples	9	83.80		
Laboratories	22	532.33	24.20	14.4*
Residual	198	332.87	1.68	

* $P < .005$

TABLE 7.96. VARIANCE COMPONENT ESTIMATES FOR LOG_e NITRATE NITROGEN DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	3.9230	(2.7999, 5.9267)	σ_R	1.9829	(1.6733, 2.4345)
σ^2_L	2.2520	(1.3025, 4.8009)	σ_L	1.5007	(1.1413, 2.1911)
σ^2*	1.6800	(1.3926, 2.0671)	σ**	1.2961	(1.1801, 1.4377)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Sodium Data Base

Data were received from 28 of the 46 laboratories that agreed to perform the sodium analysis. The analysis was performed in triplicate by 13 laboratories for all 10 leachate samples. A single value or an average value was reported by 11 laboratories. The remaining 4 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value) for this parameter, and no 0 mg/ℓ concentration levels were reported.

TABLE 7.97. SUMMARY OF ANALYTICAL RESULTS FOR SODIUM DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	16293	2200	24000	17000	421	3493
B	425	21	2360	336	17.7	420
C	2223	43	17067	1668	56.2	3514
D	666	190	1353	631	20.2	217
E	229	110	867	213	15.2	129
F	103	68	130	103	5.07	14.2
G	127	70	160	130	3.94	18.9
H	19.9	13	35	18.8	0.905	5.22
I	533	303	2387	406	7.72	413
J	58.6	0.40	330	49.3	1.63	54.5

*All entries in mg/ℓ.

A summary of the analytical results for the 10 leachate samples is given in Table 7.97 . The average sodium concentration of the samples ranged from 19.9 to 16,293 mg/ℓ, with the highest value generally 50 times larger than the lowest value for any particular leachate sample.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.63. A regression equation was calculated to be $\sigma = .0254\ \mu + .24$ with an R^2 value of 100%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .884 \log \mu - 1.20$ with an R^2 value of 96%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.73, 1.04), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. These transformed data were used in the statistical analysis of this parameter.

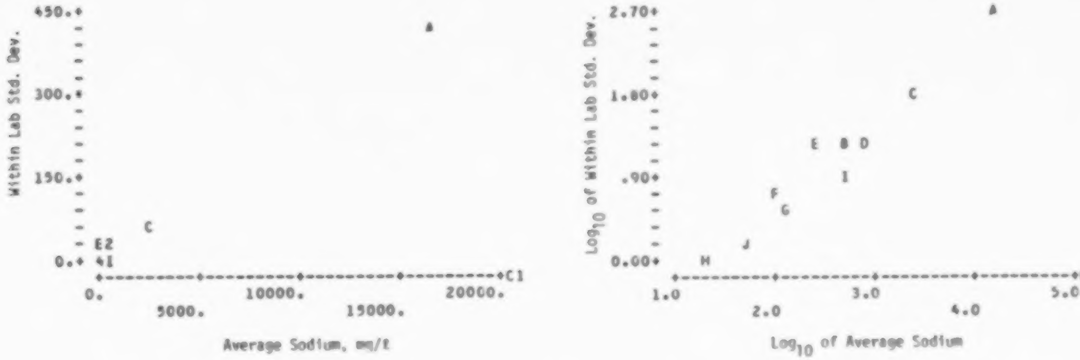

Figure 7.63. Relationship of the within laboratory standard deviation to the sodium concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.64. A regression equation was calculated to be $\sigma = .211\ \mu + 357$ with an R^2 value of 62%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.07 \log \mu - .532$ with an R^2 value of 86%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.71, 1.42), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

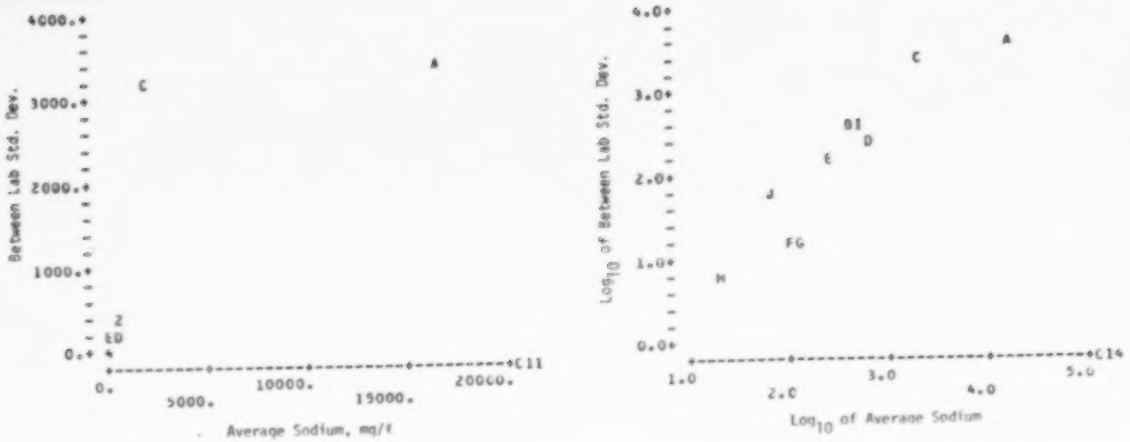

Figure 7.64. Relationship of the between laboratory standard deviation to the sodium concentration level.

The ordered laboratory averages for the sodium data plotted against the quantiles from a normal distribution are shown in Figure 7.65 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.66. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.98.

TABLE 7.98. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample A	B	C	D	E	F	G	H	I	J	Average R^2	Std. dev. of R^2
Original	68	38	29	65	38	94	87	81	44	33	58	24
Transformed	42	55	56	67	65	90	80	89	61	40	65	18

For the original data it appears that the distribution of the laboratory averages has a heavier lower tail and a heavier upper tail than the lower and upper tails of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for 7 of the 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples, however, which appear to be responsible for the low R^2 values for both the original and transformed data.

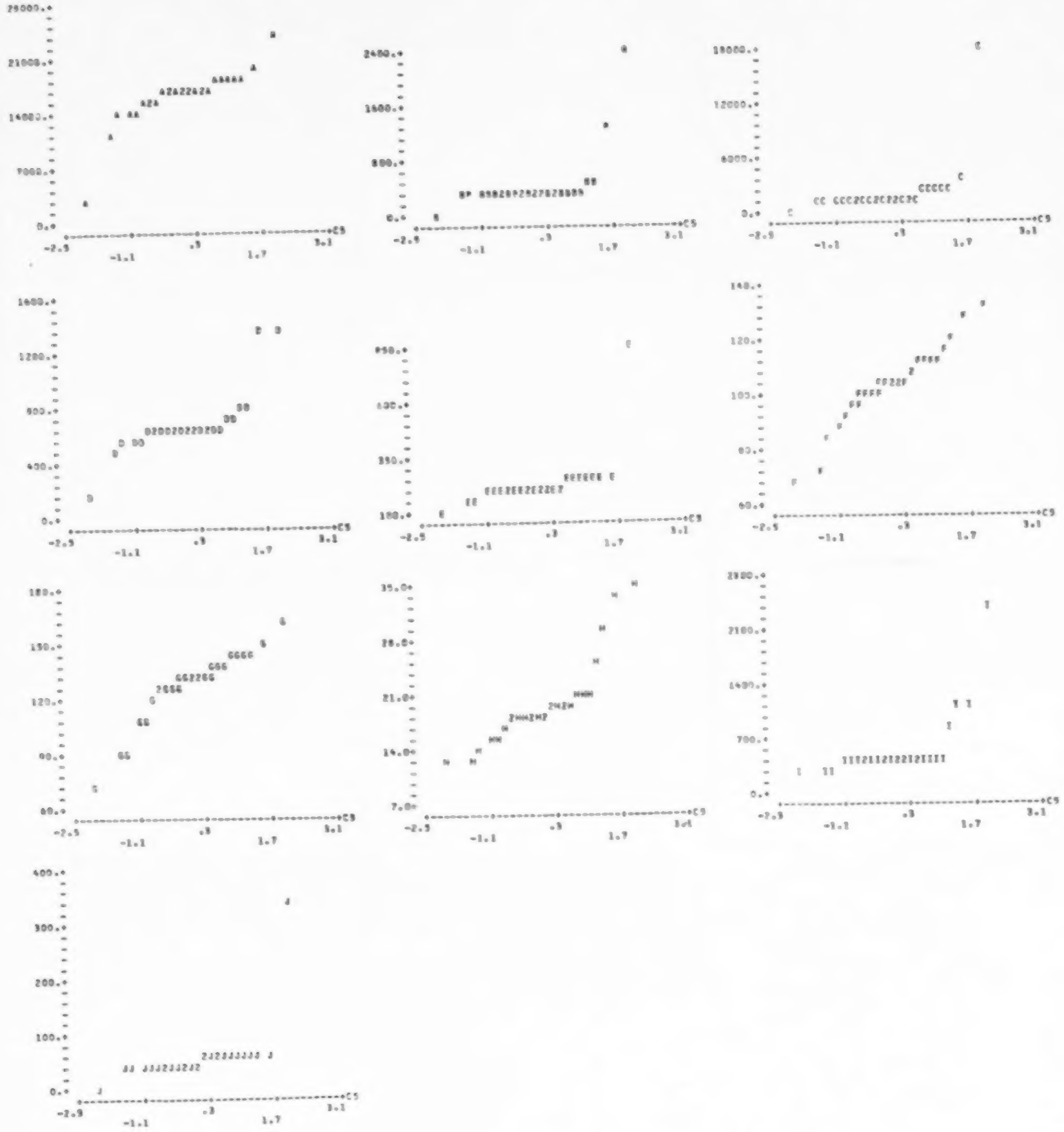

Figure 7.65. Ordered laboratory averages for sodium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

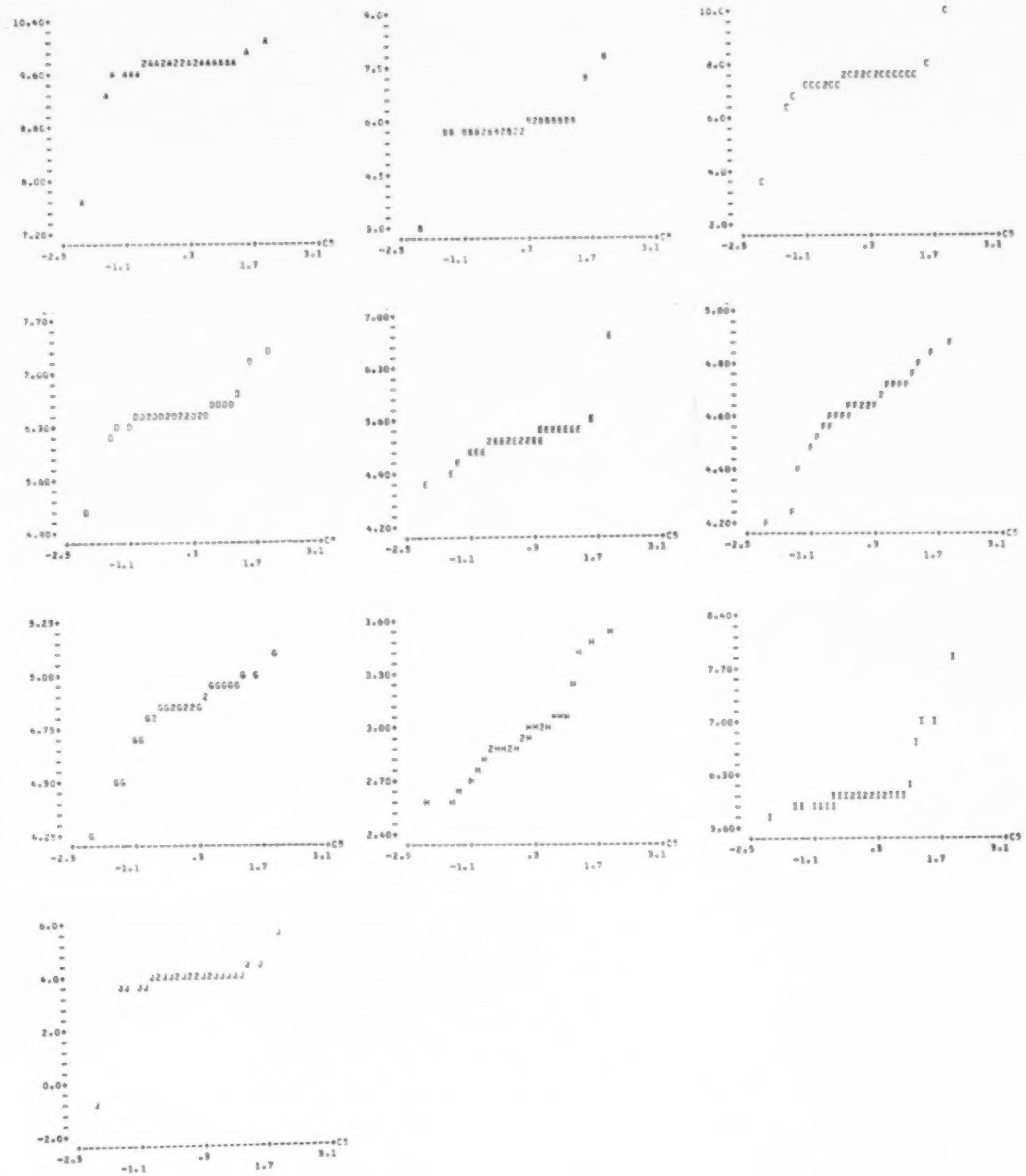

Figure 7.66. Ordered laboratory averages for $\log_e$ transformed sodium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed sodium data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 13 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.99. The hypothesis that the between laboratory variance component is zero is not rejected. The hypothesis that the laboratory sample interaction variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.100.

TABLE 7.99. ANALYSIS OF VARIANCE FOR LOG_e SODIUM DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	389	1472.518	--	--
Leachate Samples	9	1350.0216	--	--
Laboratories	12	13.8111	1.1509	1.15*
Lab x Sample	108	108.3325	1.0031	717 **
Residual	260	.3528	.0014	--

* $P > .25$

** $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.101. The hypothesis that the between laboratory variance component is zero is rejected. The variance component estimates obtained for this data set are given in Table 7.102.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .12$, $\sigma_L = .065$, and $\sigma = .10$. These values are considerably smaller than the corresponding estimates given in Table 7.102, which indicates that greater precision may be attainable.

TABLE 7.100 VARIANCE COMPONENT ESTIMATES FOR LOG_e SODIUM DATA BASED ON LABORATORIES REPORTING THREE REPLICATES

	Estimate		Estimate
σ^2_L	.3402	σ_L	.5833
σ^2_{LPLS}	.3388	σ_{LPLS}	.5821
σ^2_L	.0049	σ_L	.0702
σ^2_{LS}	.3339	σ_{LS}	.5778
σ^2_W	.0014	σ_W	.0374

TABLE 7.101 ANALYSIS OF VARIANCE FOR LOG_e SODIUM DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	279	982.910		
Leachate Samples	9	902.841		
Laboratoires	27	11.773	.436	1.55*
Residual	243	68.296	.281	

* $.025 < P < .05$

TABLE 7.102. VARIANCE COMPONENT ESTIMATES FOR LOG_e SODIUM DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.2965	(.2517, .3544)	σ_R	.5445	(.5017, .5953)
σ^2_L	.0155	(.0051, .1824)	σ_L	.1245	(.0717, .4271)
σ^2*	.2810	(.2370, .3385)	σ**	.5301	(.4869, .5818)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Potassium Data Base

Data were received from 29 of the 44 laboratories that agreed to perform the potassium analysis. The analysis was performed in triplicate by 14 laboratories for all 10 leachate samples. A single value or an average value was reported by 10 laboratories. The remaining 5 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value) for this parameter, and no 0 mg/ℓ concentration levels were reported.

TABLE 7.103 SUMMARY OF ANALYTICAL RESULTS FOR POTASSIUM DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	723	13.6	1090	757	38.8	239
B	270	11.4	580	281	21.1	98.5
C	861	4.8	1335	924	40.9	288
D	320	100	413	345	10.3	86.8
E	161	53	218	167	11	36.9
F	83	30	123	84	2.99	20.3
G	116	24	154	120	3.71	28.9
H	25.5	5	275	12.7	0.55	52.8
I	241	90	580	232	6.97	74.1
J	13.8	3.3	85	11.6	1.1	14

*All entries in mg/ℓ.

A summary of the analytical results for the 10 leachate samples is given in Table 7.103. The average potassium concentration of the samples ranged from 13.8 to 861 mg/ℓ, with the highest value generally 25 times larger than the lowest value for any particular leachate sample.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.67. A regression equation was calculated to be $\sigma = .0475\ \mu - .14$ with an R^2 value of 94%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .93 \log \mu - 1.19$ with an R^2 value of 93%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.72, 1.14), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. These transformed data were used in the statistical analysis of this parameter.

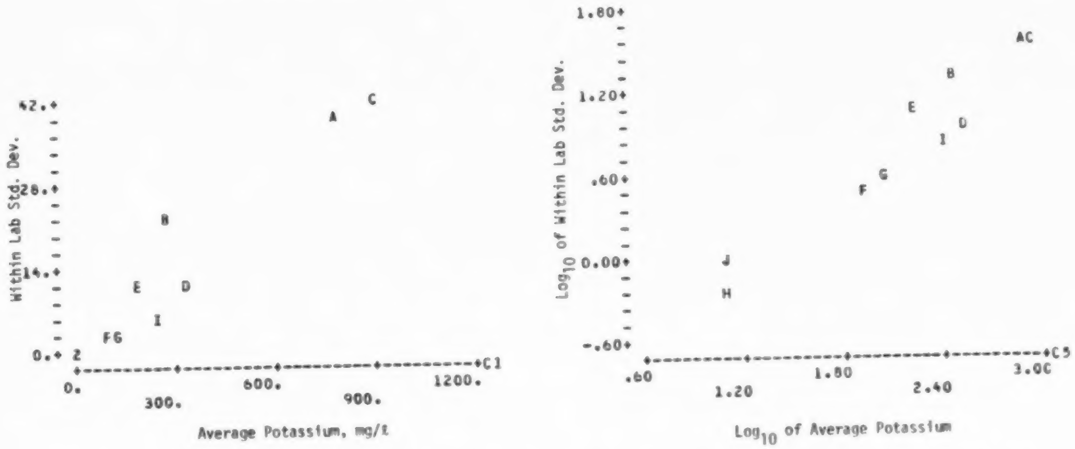

Figure 7.67. Relationship of the within laboratory standard deviation to the potassium concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.68. A regression equation was calculated to be $\sigma = .321\ \mu + 3.69$ with an R^2 value of 96%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .633 \log \mu + .400$ with an R^2 value of 72%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.31, .96), which suggests that a square root or perhaps logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

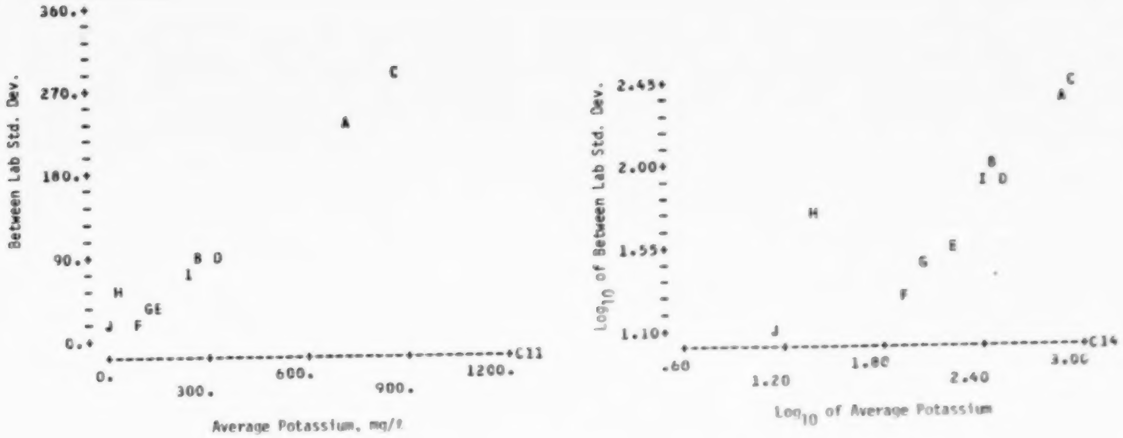

Figure 7.68. Relationship of the between laboratory standard deviation to the potassium concentration level.

The ordered laboratory averages for the potassium data plotted against the quantiles from a normal distribution are shown in Figure 24.3 for the ten leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 24.4 . The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 24.2.

TABLE 7.104. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

	Leachate Sample										Average R^2	Std. dev. of R^2
Data	A	B	C	D	E	F	G	H	I	J		
Original	80	71	71	84	86	91	84	30	54	32	67	22
Transformed	47	47	40	64	73	80	62	59	65	67	60	12

For the original data it appears that the distribution of the laboratory averages has a heavier lower tail and a heavier upper tail than the lower and upper tails of a normal distribution. The distribution of the $\log_e$ transformed data appears less similar to a normal distribution than the distribution of the original data (i.e., further from a straight line). This observation is supported by the lower R^2 values for 7 of the 10 leachate samples and the lower average R^2 for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples however, which appear to be responsible for the low R^2 values for both the original and transformed data. Perhaps these data should be reanalyzed by converting the reported results into percentages of the sample average concentrations.

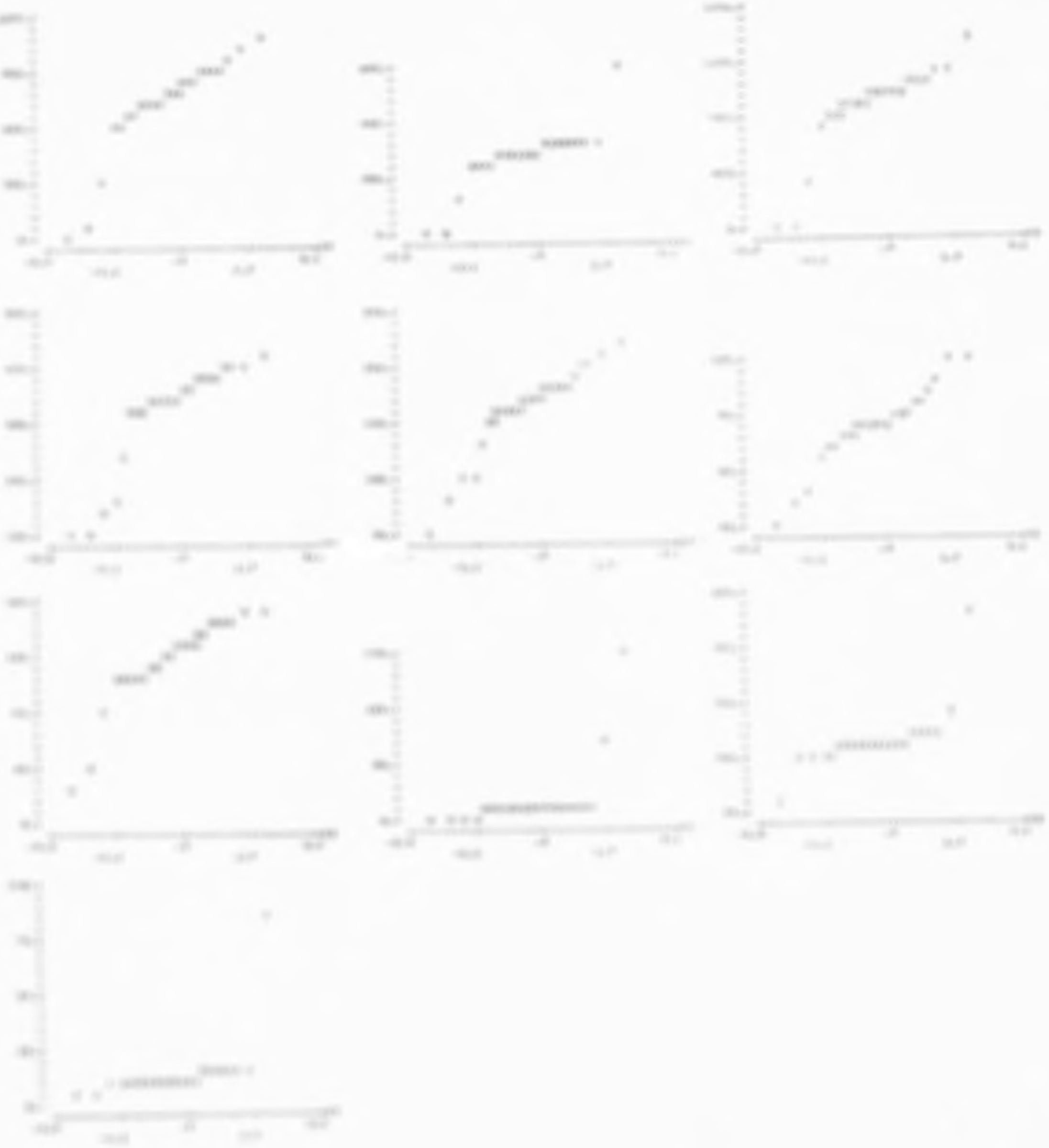

Figure 7.69. Ordered laboratory averages for potassium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

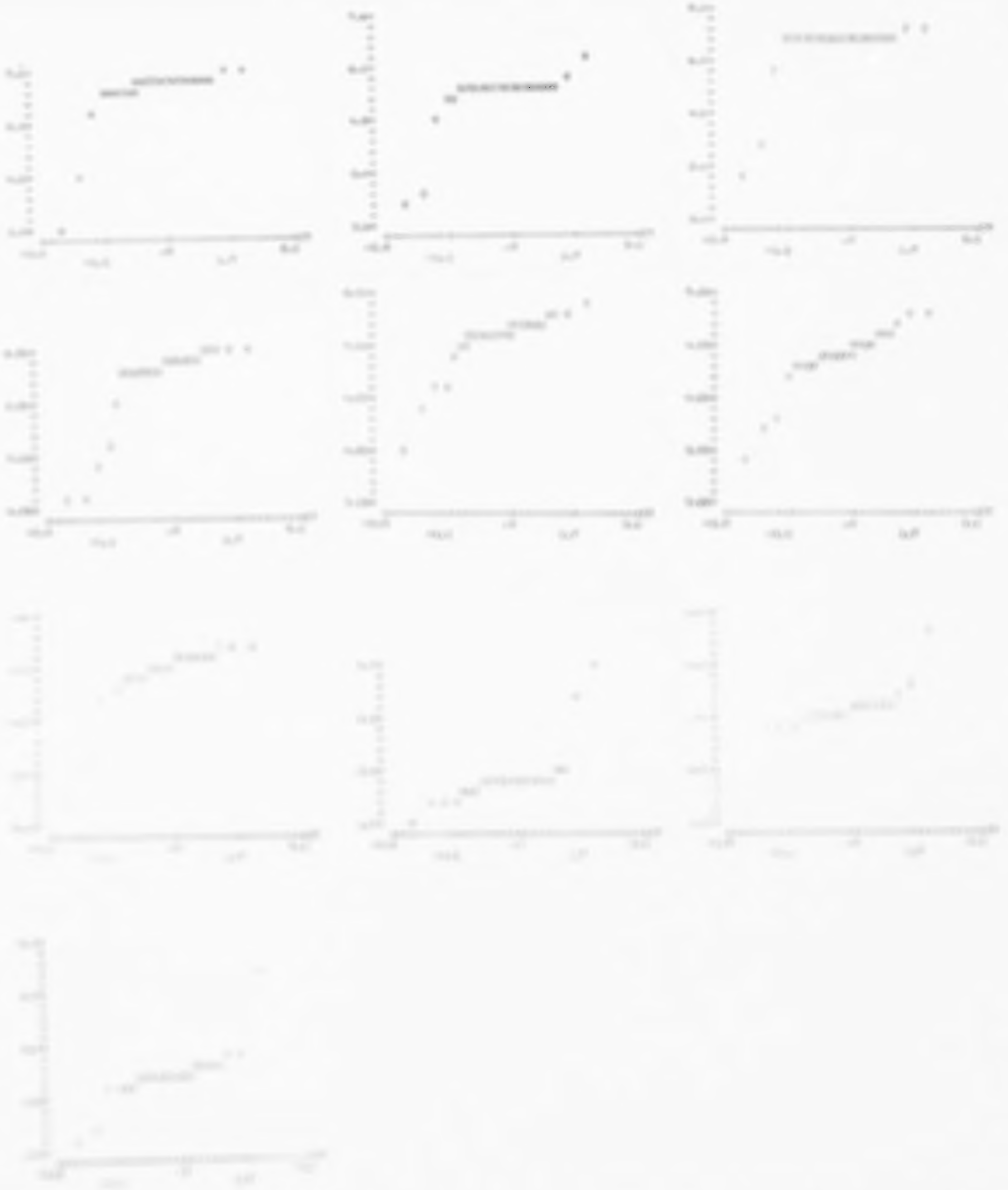

Figure 7.70. Ordered laboratory averages for $\log_{10}$ transformed potassium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed potassium data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

TABLE 7.105. ANALYSIS OF VARIANCE FOR LOG_e POTASSIUM DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	419	909.31441	--	--
Leachate Samples	9	770.98492	--	--
Laboratories	13	69.68081	5.36006	9.26*
Lab x Sample	117	67.75832	.57913	182 *
Residual	280	.89036	.00318	--

* $P < .005$

The data from 14 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.105. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.106.

TABLE 7.106. VARIANCE COMPONENT ESTIMATES FOR LOG_e POTASSIUM DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.3545	(.2450, .5587)	σ_R	.5954	(.4950, .7475)
σ^2_{LPLR}	.3513	(.2421, .5560)	σ_{LPLR}	.5927	(.4921, .7457)
σ^2_L	.1594	(.0785, .4801)	σ_L	.3992	(.2802, .6929)
σ^2_{LR}	.1920	(.1507, .2529)	σ_{LR}	.4382	(.3882, .5029)
σ^2_W	.0032	(.0027, .0038)	σ_W	.0564	(.0521, .0615)

TABLE 7.107 ANALYSIS OF VARIANCE FOR LOG_e POTASSIUM DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	289	624.248		
Leachate Samples	9	501.875	55.764	
Laboratories	28	50.206	1.793	6.27*
Residual	252	72.166	.286	

* $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.107. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.108.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .16$, $\sigma_L = .12$, and $\sigma = .11$. These values are considerably smaller than the corresponding estimates given in Table 7.108 which indicates that greater precision may be attainable.

TABLE 7.108. VARIANCE COMPONENT ESTIMATES FOR LOG_e POTASSIUM DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.4367	(.3488, .629)	σ_R	.6608	(.5906, .7932)
σ^2_L	.1507	(.0879, .316)	σ_L	.3882	(.2965, .5624)
σ^2*	.2860	(.2420, .343)	σ**	.5348	(.4919, .5859)

* $\sigma^2 = \sigma^2_{LR} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LR} + \sigma^2_W}$

Calcium Data Base

Data were received from 28 of the 46 laboratories that agreed to perform the calcium analysis. The analysis was performed in triplicate by 13 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 10 laboratories. The remaining 4 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value) for this parameter, and no 0 mg/ℓ concentration levels were reported.

TABLE 7.109. SUMMARY OF ANALYTICAL RESULTS FOR CALCIUM DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	2832	1250	13600	2468	239	2171
B	2110	237	45000	506	521	8409
C	910	95	5354	709	194	949
D	626	337	6245	409	188	1103
E	698	307	7900	433	13.6	1413
F	675	282	7413	408	64.4	1323
G	683	159	8300	406	45.4	1496
H	334	11	5944	135	263	1100
I	692	44.9	15976	136	32.8	2996
J	470	12	10400	109	49.2	1946

*All entries in mg/ℓ.

A summary of the analytical results for the 10 leachate samples is given in Table 7.109. The average calcium concentration of the samples ranged from 334 to 2832 mg/ℓ, with the highest value generally 200 times larger than the lowest value for any particular leachate sample.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.71. A regression equation was calculated to be $\sigma = .123\ \mu + 13.5$ with an R^2 value of 53%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .853 \log \mu - .57$ with an R^2 value of 21%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (-.52, 2.23), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

Although transformations were indicated to stabilize the within and between laboratory variances, the appearance of the graphs and low R^2 values makes the choice of a transformation uncertain. The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. These transformed data were used in the statistical analysis of this parameter.

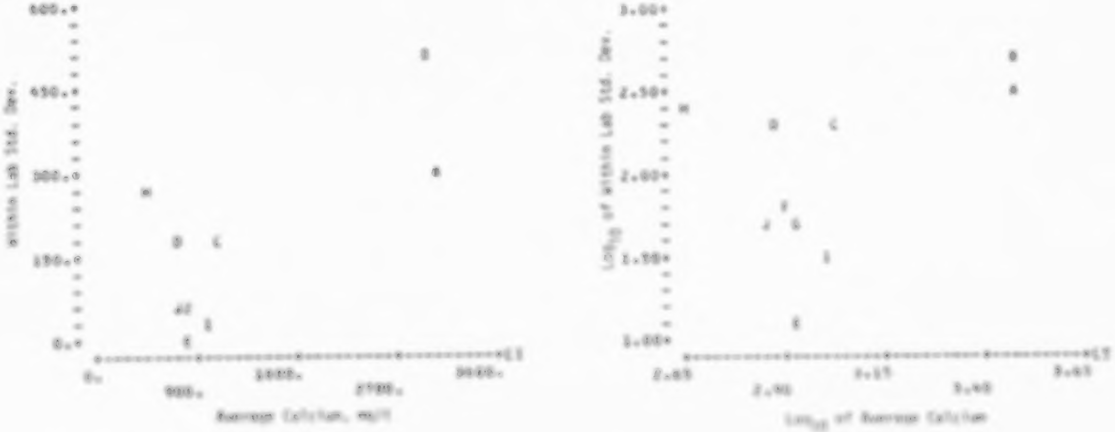

Figure 7.71. Relationship of the within laboratory standard deviation to the calcium concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.72. A regression equation was calculated to be $\sigma = 1.49\ \mu + 795$ with an R^2 value of 29%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .506 \log \mu + 1.55$ with an R^2 value of 34%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (-.08, 1.25), which suggests that a square root or logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

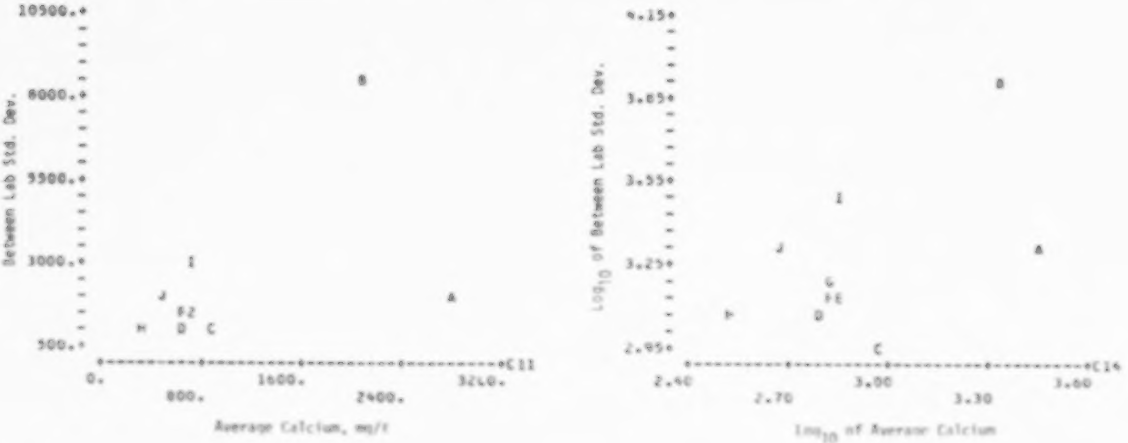

Figure 7.72. Relationship of the between laboratory standard deviation to the calcium concentration level.

The ordered laboratory averages for the calcium data plotted against the quantiles from a normal distribution are shown in Figure 7.73 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.74. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.110

TABLE 7.110. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average R^2	Std. dev. of R^2
	A	B	C	D	E	F	G	H	I	J		
Original	36	18	39	20	19	21	21	19	17	17	23	8
Transformed	67	51	65	37	35	46	54	51	43	43	49	11

The graphs for the original data are of little value in determining the shape of their distribution due to an extremely outlying result in all 10 leachate samples. The distribution of the $\log_e$ transformed data could be closer to that of a normal distribution than the distribution of the original data. This conjecture is supported by the higher R^2 values for all 10 leachate samples and the greater average R^2 $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in most of the leachate samples, however, which appear to be responsible for the low R^2 values for both the original and transformed data.

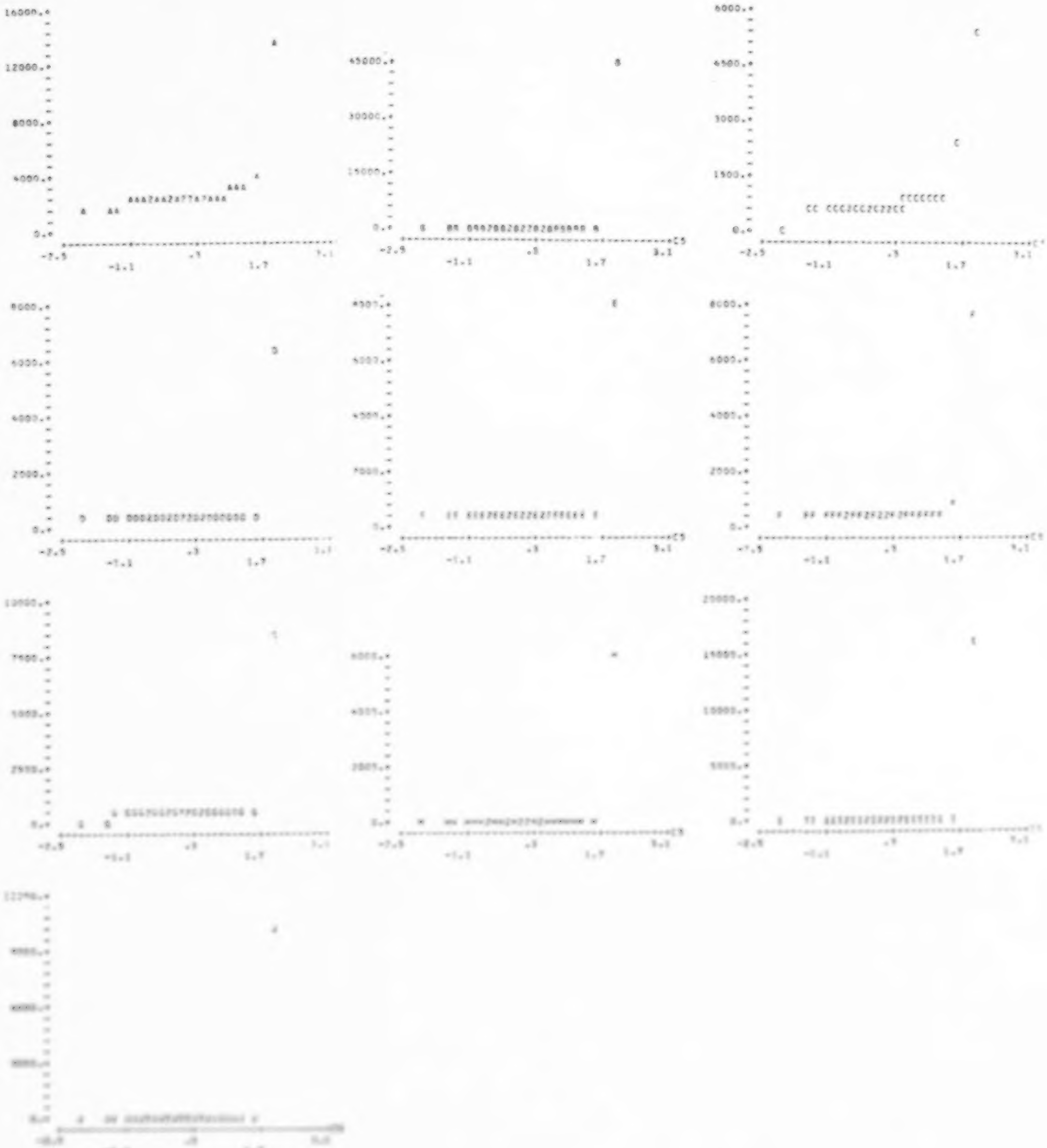

Figure 7.73. Ordered laboratory averages for calcium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

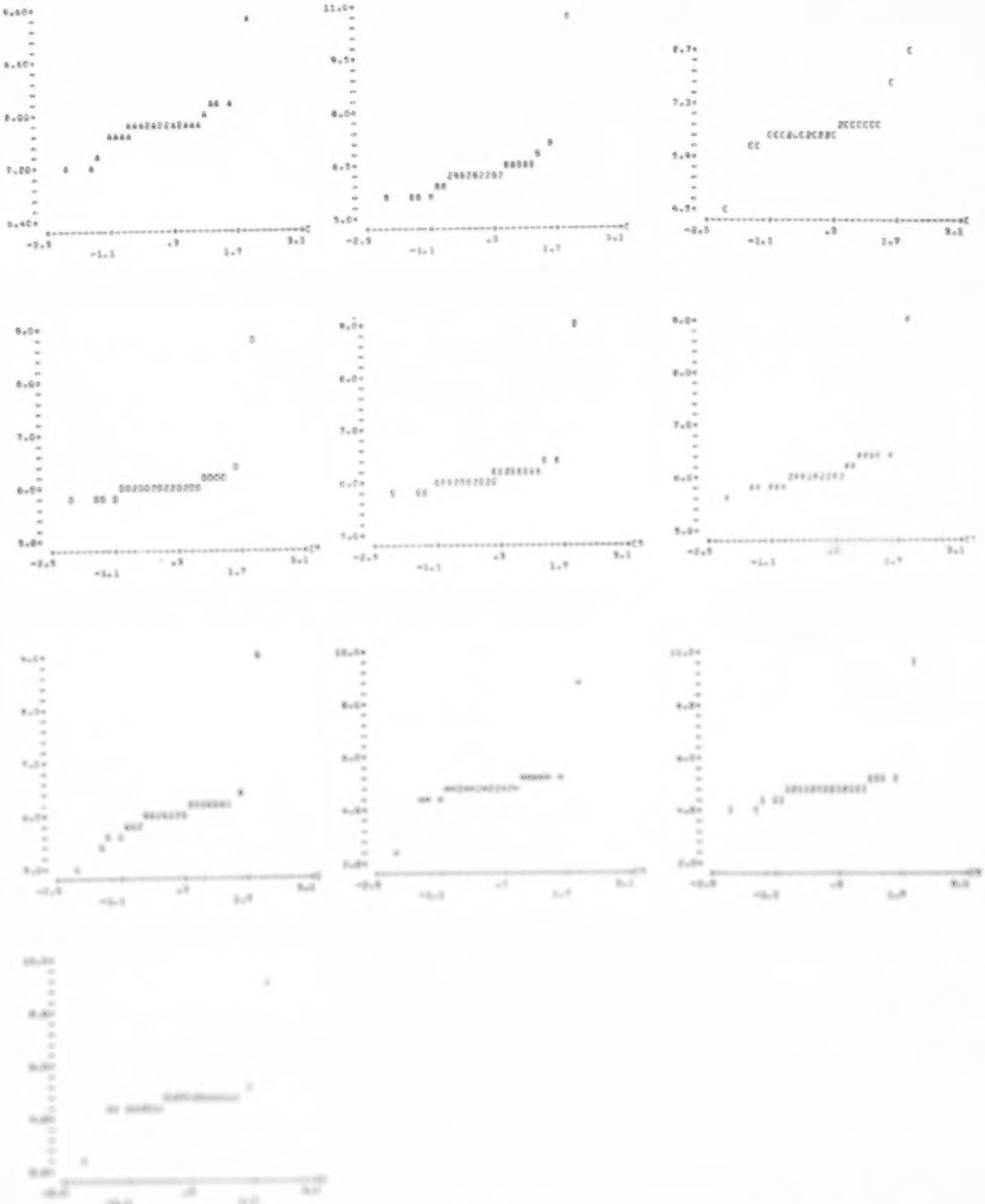

Figure 7.76. Ordered laboratory averages for $\log_e$ transformed calcium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed calcium data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 13 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.111. The hypothesis that the between laboratory variance component is zero is not rejected. The hypothesis that the laboratory sample interaction variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.112.

TABLE 7.111. ANALYSIS OF VARIANCE FOR LOG_e CALCIUM DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	389	371.96375	--	--
Leachate Samples	9	328.87956	--	--
Laboratories	12	5.74678	.4789	1.41*
Lab x Sample	108	36.78483	.3406	160 **
Residual	260	.55253	.00213	--

* $.1 < P < .25$

** $P < .005$

TABLE 7.112. VARIANCE COMPONENT ESTIMATES FOR LOG_e CALCIUM DATA BASED ON LABORATORIES REPORTING THREE REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.1196	(.0940, .1571)	σ_R	.3458	(.3067, .3964)
σ^2_{LPLS}	.1174	(.0923, .1545)	σ_{LPLS}	.3427	(.3038, .3930)
σ^2_L	.0046	(.0009, 6.7983)	σ_L	.0679	(.0299, 2.6074)
σ^2_{LS}	.1128	(.0878, .1505)	σ_{LS}	.3359	(.2962, .3879)
σ^2_W	.0021	(.0018, .0025)	σ_W	.0462	(.0425, .0505)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.113. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.114.

TABLE 7.113 ANALYSIS OF VARIANCE FOR LOG_e CALCIUM DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	279	364.911	--	--
Leachate Samples	9	217.163	--	--
Laboratories	27	114.963	4.258	31.5*
Residual	243	32.785	.135	--

* $P < .005$

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .23$, $\sigma_L = .12$, and $\sigma = .20$. These values are considerably smaller than the corresponding estimates given in Table 7.114, which indicates that greater precision may be attainable.

TABLE 7.114. VARIANCE COMPONENT ESTIMATES FOR LOG_e CALCIUM DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf Int.		Estimate	95% Conf. Int.
σ^2_R	.5473	(.3754, 8725)	σ_R	.7398	(.6127, .9341)
σ^2_L	.4123	(.2542, 7823)	σ_L	.6421	(.5042, .8845)
σ^2*	.1350	(.1139, 1626)	σ**	.3674	(.3375, .4033)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Magnesium Data Base

Data were received from 27 of the 46 laboratories that agreed to perform the magnesium analysis. The analysis was performed in triplicate by 12 laboratories for all 10 leachate samples. A single value or an average value was reported by 11 laboratories. The remaining 4 laboratories reported an unequal number of replicates.

One 2 mg/ℓ value was reported as a detection limit (i.e., < value) for leachate sample J. Half the reported detection limit value was used in the data base for all statistical analyses. One 0 mg/ℓ concentration level for leachate sample J was reported.

TABLE 7.115 SUMMARY OF ANALYTICAL RESULTS FOR MAGNESIUM DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	363	138	800	347	12.8	106
B	158	64.9	300	150	4.6	39
C	328	6.5	600	358	9.78	130
D	180	141	267	178	15.8	24.6
E	99.6	18.7	250	92.7	2.74	36.6
F	60.7	50	93.5	58.3	2.5	9.83
G	66.6	36.3	110	64.3	2.04	14.5
H	19.3	7.5	180	8.87	.791	36.3
I	191	10.2	232	194	4.04	42.4
J	15.5	0	153	7.4	1.4	31.5

*All entries in mg/ℓ

A summary of the analytical results for the 10 leachate samples is given in Table 7.115. The average magnesium concentration of the samples ranged from 15.5 to 363 mg/ℓ, with the highest value generally 20 times larger than the lowest value for any particular leachate sample.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.75. A regression equation was calculated to be $\sigma = .0327\ \mu + .68$ with an R^2 value of 58%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .892 \log \mu - 1.23$ with an R^2 value of 82%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.55, 1.24), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within laboratory variance. Before applying the transformation, .5 was added to all zero values. Although the square root transformation was indicated to stabilize the between laboratory variance, the appearance of the graphs and low R^2 value makes the choice of the logarithmic transformation seem reasonable. The logarithmic transformed data were used in the statistical analysis of this parameter.

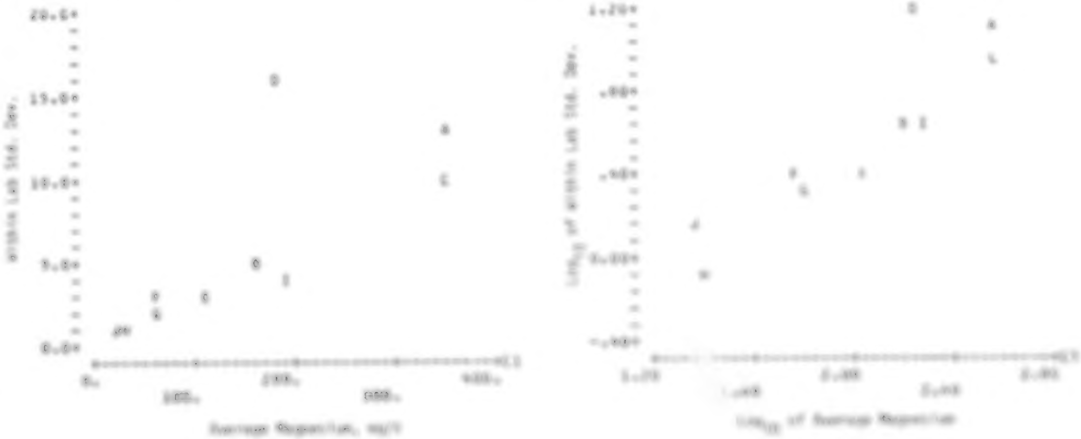

Figure 7.75. Relationship of the within laboratory standard deviation to the magnesium concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.76. A regression equation was calculated to be $\sigma = .275\ \mu + 6.3$ with an R^2 value of 73%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .304 \log \mu + .788$ with an R^2 value of 29%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (-.11, .80), which suggests that a square root transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

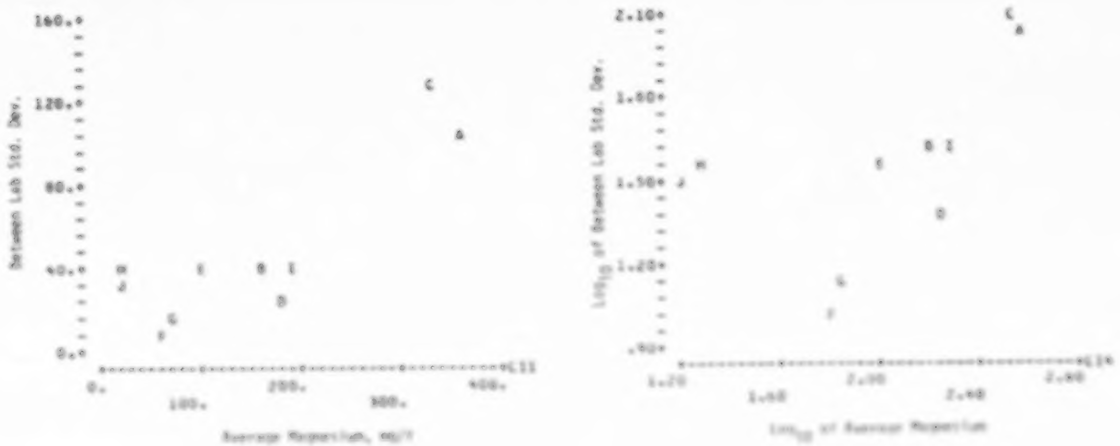

Figure 7.76. Relationship of the between laboratory standard deviation to the magnesium concentration level.

The ordered laboratory averages for the magnesium data plotted against the quantiles from a normal distribution are shown in Figure 7.77 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.78. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.116.

TABLE 7.116. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample A	B	C	D	E	F	G	H	I	J	Average R^2	Std. dev. of R^2
Original	65	76	78	82	60	79	87	32	68	33	66	19
Transformed	72	78	50	89	60	86	87	51	33	64	67	19

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for 6 of the 10 leachate samples and the slightly greater average R^2 for the $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

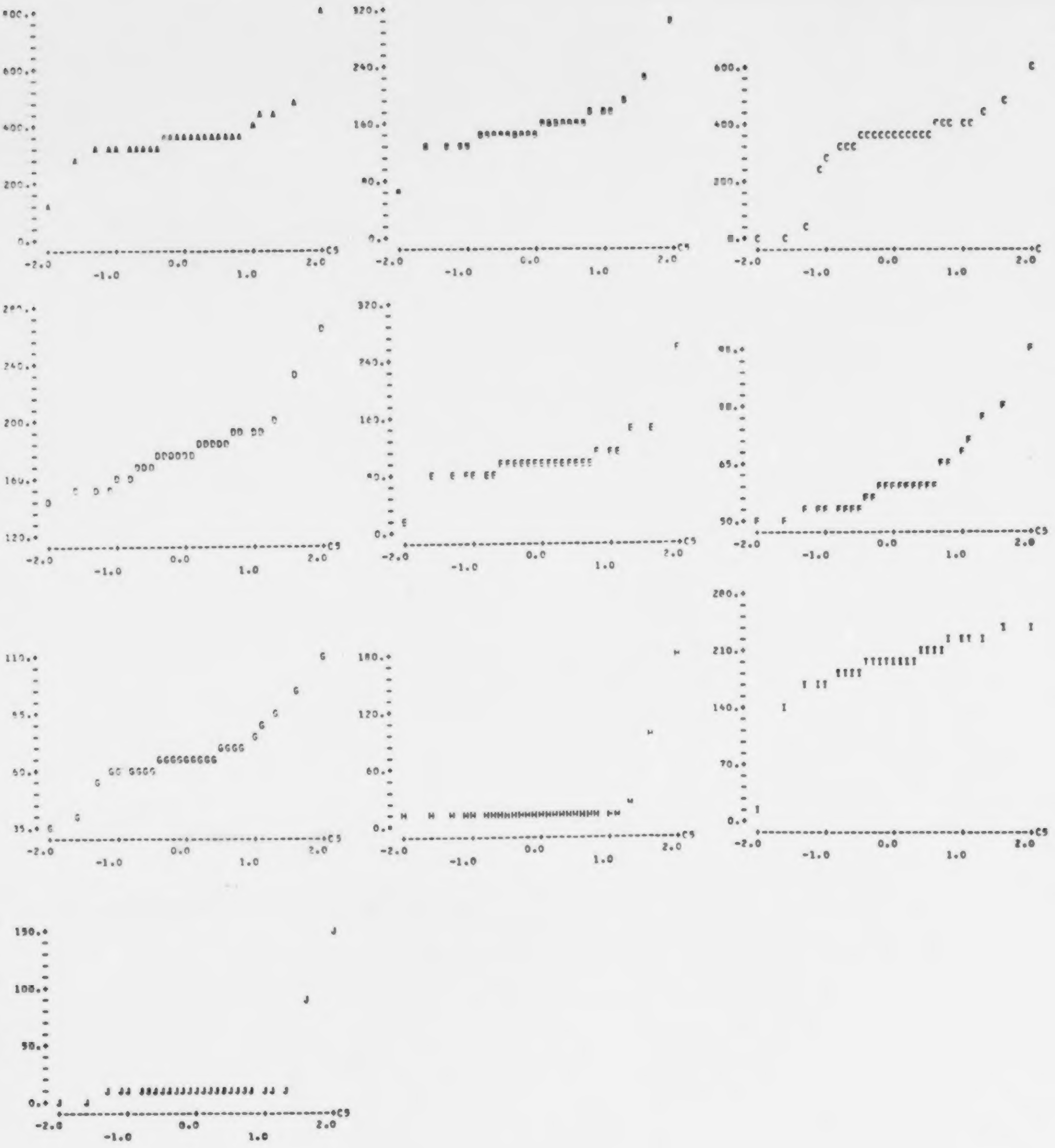

Figure 7.77. Ordered laboratory averages for magnesium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

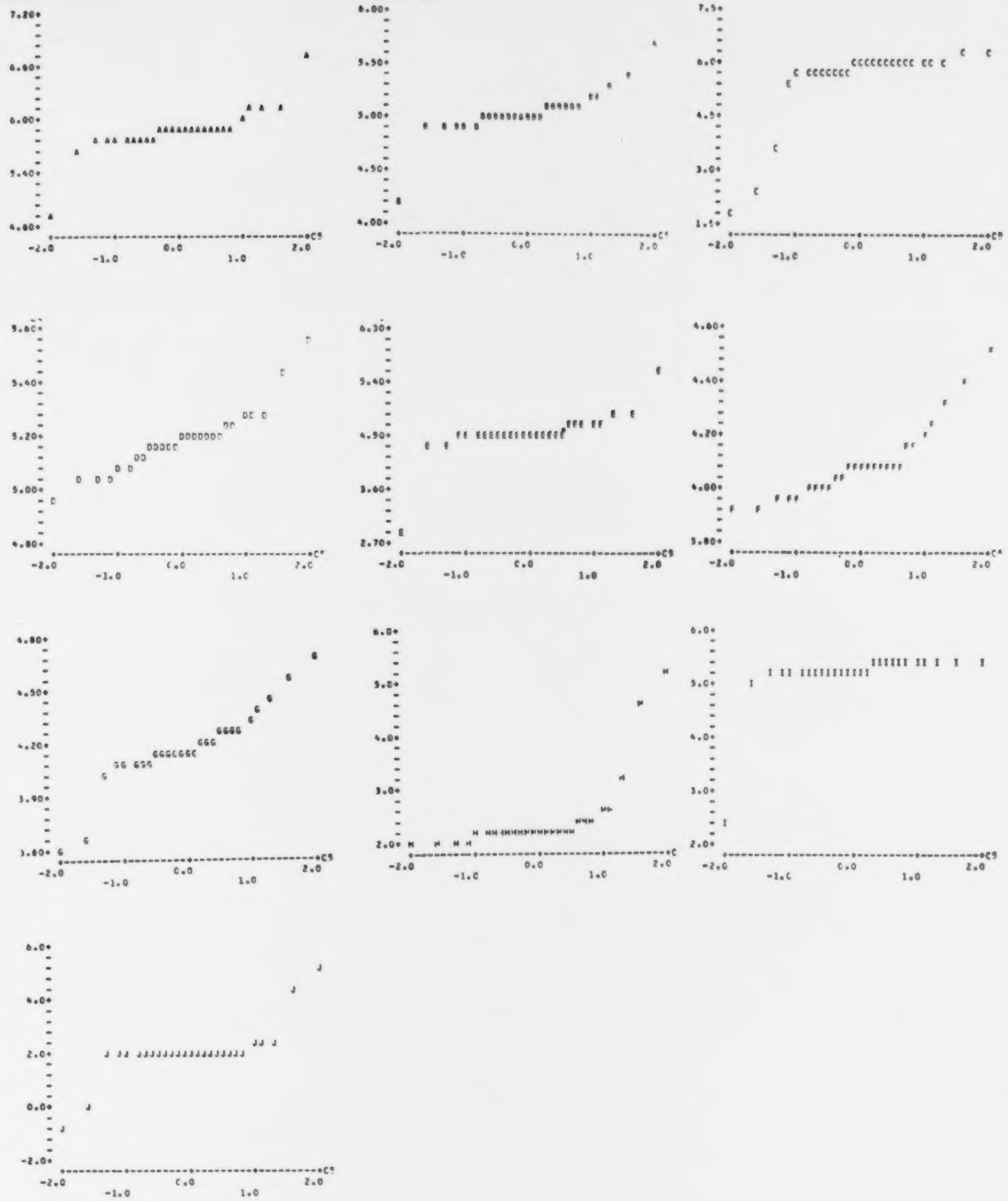

Figure 7.78. Ordered laboratory averages for $\log_e$ transformed magnesium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed magnesium data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 12 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.117. The hypothesis that the between laboratory variance component is zero is not rejected. The hypothesis that the laboratory sample interaction variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.118.

TABLE 7.117. ANALYSIS OF VARIANCE FOR LOG_e MAGNESIUM DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	359	588.5731	--	--
Leachate Samples	9	442.68331	--	--
Laboratories	11	9.73885	.88535	.65 *
Lab x Sample	99	135.84776	1.3722	1089**
Residual	240	.30318	.00126	--

* $P > .25$
** $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.119 The hypothesis that the between laboratory variance component is zero is not rejected. The variance component estimates obtained for this data set are given in Table 7.120

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .10$, $\sigma_L = .077$, and $\sigma = .064$. These values are considerably smaller than the corresponding estimates given in Table 7.120, which indicates that greater precision may be attainable.

TABLE 7.118 VARIANCE COMPONENT ESTIMATES FOR LOG_e MAGNESIUM DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate		Estimate
σ^2_L	.4420	σ_L	.6648
σ^2_{LPLS}	.4408	σ_{LPLS}	.6639
σ^2_L	*	σ_L	*
σ^2_{LS}	.4570	σ_{LS}	.6760
σ^2_W	.0013	σ_W	.0355

* The estimate of the between laboratory variance component was negative.

TABLE 7.119 ANALYSIS OF VARIANCE FOR LOG_e MAGNESIUM DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	269	481.702	--	--
Leachate Samples	9	389.935	--	--
Laboratories	26	11.924	.459	1.35*
Residual	234	79.843	.341	--

* $.1 < p < .25$

TABLE 7.120. VARIANCE COMPONENT ESTIMATES FOR LOG_e MAGNESIUM DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.3528	(.2990, .4227)	σ_R	.5940	(.5468, .6501)
σ^2_L	.0118	(.0029, .9871)	σ_L	.1086	(.0540, .9935)
σ^2*	.3410	(.2868, .4123)	σ**	.5840	(.5355, .6421)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Barium Data Base

Data were received from 18 of the 43 laboratories who agreed to perform the barium analysis. The analysis was performed in triplicate by 8 laboratories for all 10 leachate samples. A single value or an average value was reported by 9 laboratories. The remaining laboratory reported an unequal number of replicates.

A summary of the analytical results for the 10 leachate samples is given in Table 7.121 . The average barium concentration of the samples ranged from .918 to 44.2 mg/ℓ, with the highest value generally 500 times larger than the lowest value for any particular leachate sample.

TABLE 7.121. SUMMARY OF ANALYTICAL RESULTS FOR BARIUM DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	44.2	.1	713	.793	32.6	172
B	3	.0667	29.7	.8	14	6.86
C	2.87	.0667	31.7	.6	12.9	7.47
D	7.46	4.0	25.4	6.1	1.44	5.13
E	2.05	0.0	10	1.43	.223	2.15
F	1.87	.05	22.8	.287	2.02	5.35
G	1.32	0.0	17.2	.258	2.38	3.99
H	1.44	0.0	12.6	.2	.658	3.62
I	1.75	.1	17.3	.333	2.86	4.29
J	.918	0.0	7.8	.143	2.79	2.2

*All entries in mg/ℓ.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.79. A regression equation was calculated to be $\sigma = .326\ \mu + 3.19$ with an R^2 value of 78%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .793 \log \mu - .025$ with an R^2 value of 43%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.05, 1.54), which suggests that a square root or logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

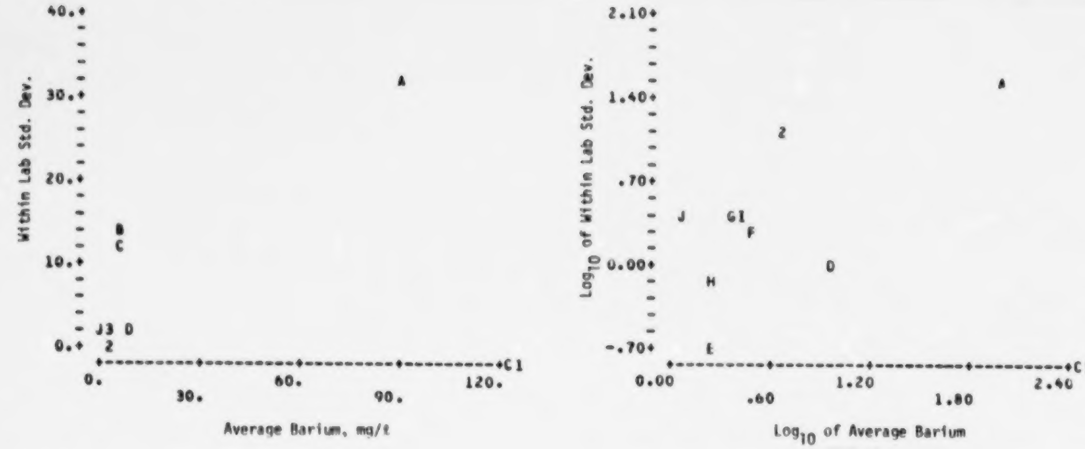

Figure 7.79. Relationship of the within laboratory standard deviation to the barium concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.80. A regression equation was calculated to be $\sigma = 3.96\ \mu - 5.12$ with an R^2 value of 98%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.01 \log \mu + .329$ with an R^2 value of 82%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.63, 1.39), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

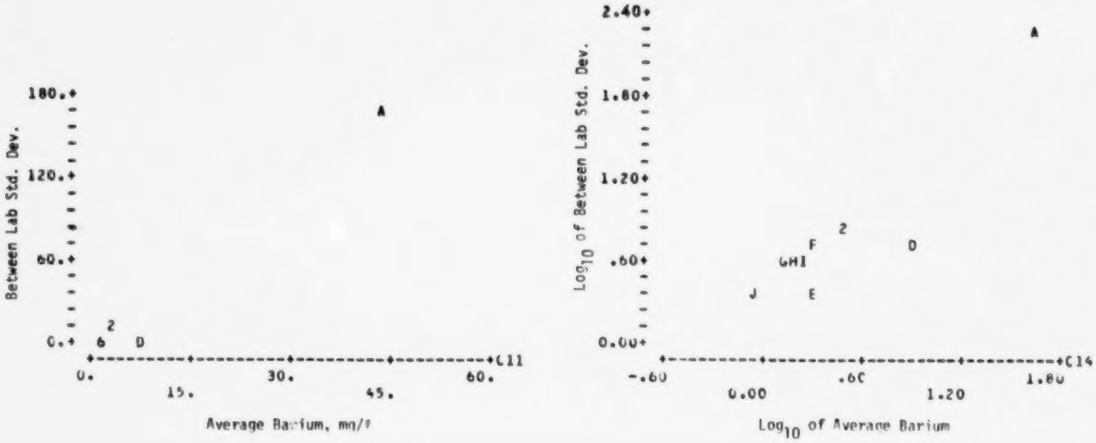

Figure 7.80 Relationship of the between laboratory standard deviation to the barium concentration level.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the between laboratory variance. Before applying the transformation, .025 was added to all zero values. Although the square root or logarithmic transformation was indicated to stabilize the within laboratory variance, the appearance of the graphs and low R^2 value makes the choice of a transformation uncertain. The logarithmic transformed data were used in the statistical analysis of this parameter.

The ordered laboratory averages for the barium data plotted against the quantiles from a normal distribution are shown in Figure 7.81 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.82. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.122

TABLE 7.122. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

	Leachate Sample										Average	Std. dev.
Data	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	25	39	37	57	48	34	30	40	20	42	37	11
Transformed	84	92	89	78	71	87	91	74	83	81	83	7

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data, (i.e. closer to a straight line). This observation is supported by the higher R^2 values for all 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed barium data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 8 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.123. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance

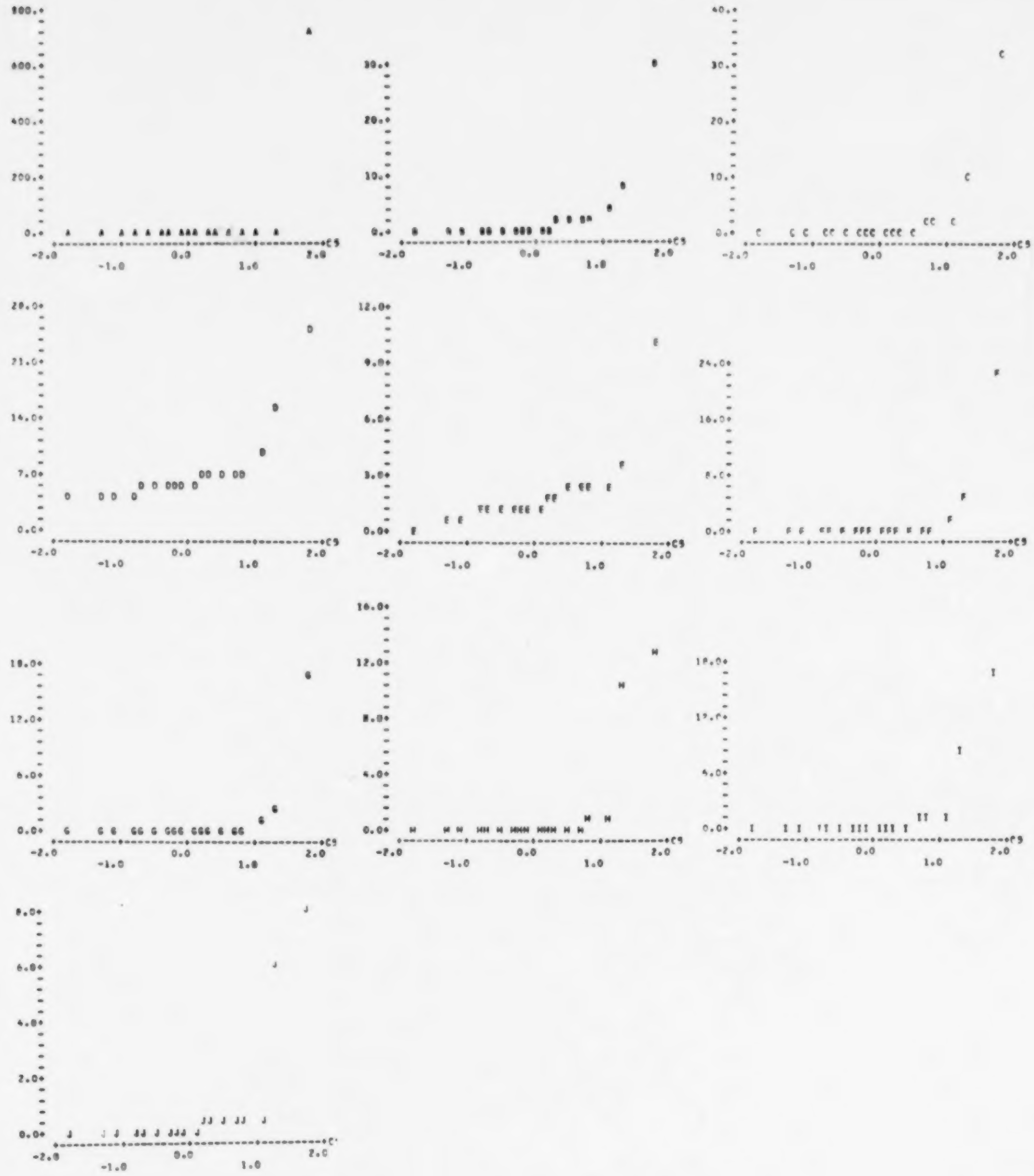

Figure 7.81. Ordered laboratory averages for barium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

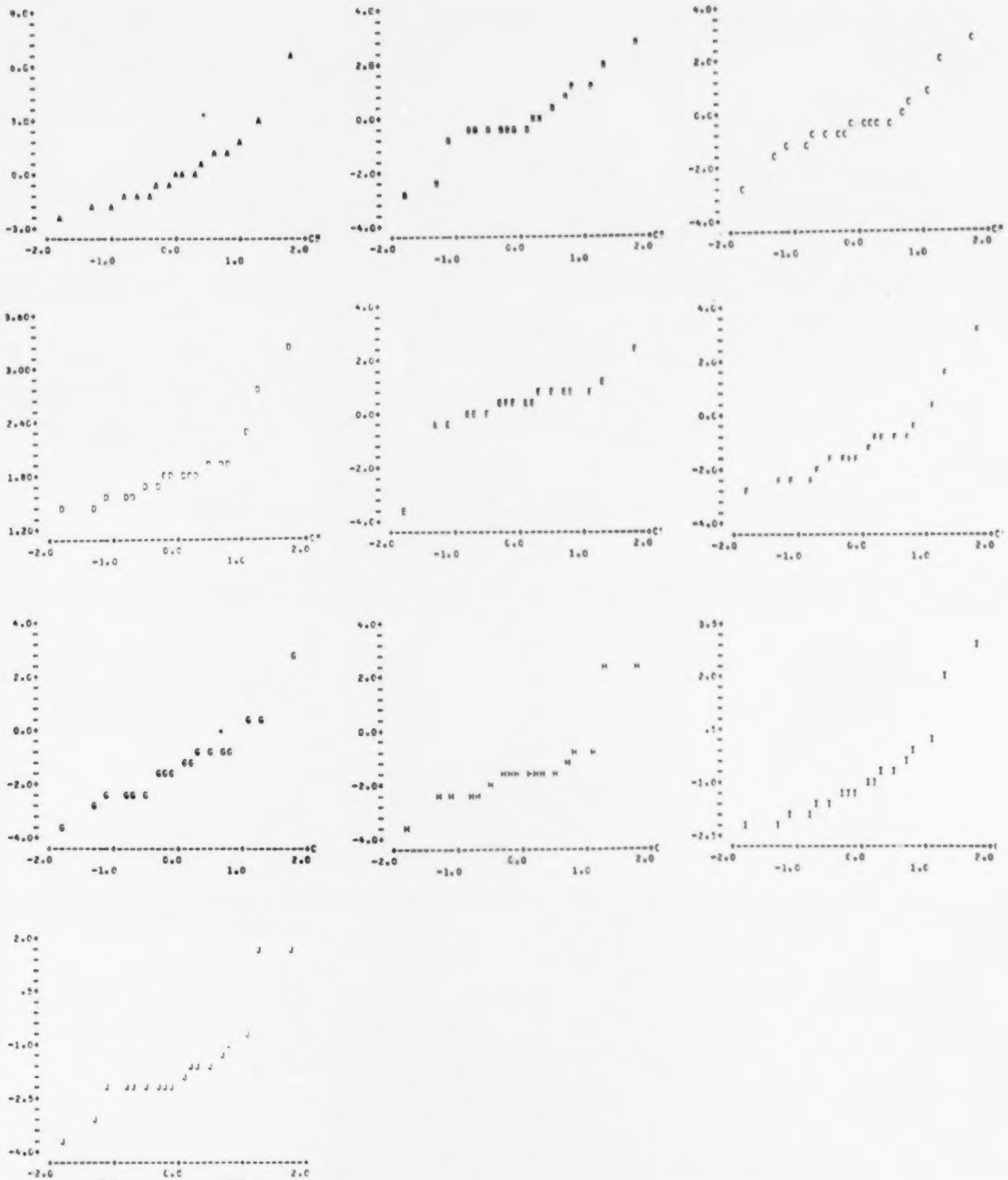

Figure 7.82. Ordered laboratory averages for $\log_e$ transformed barium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.124.

TABLE 7.123. ANALYSIS OF VARIANCE FOR LOG_e BARIUM DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	239	881.572	--	--
Leachate Samples	9	226.432	--	--
Laboratories	7	345.672	49.382	11.1*
Lab x Sample	63	279.684	4.439	23.9*
Residual	160	29.784	.186	--

* $P < .005$

TABLE 7.124 VARIANCE COMPONENT ESTIMATES FOR LOG_e BARIUM DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	3.1018	(1.8755, 6.0904)	σ_R	1.7612	(1.3695, 2.4679)
σ^2_{LPLS}	2.9158	(1.7152, 6.0217)	σ_{LPLS}	1.7076	(1.3097, 2.4539)
σ^2_L	1.4981	(.6143, 7.5573)	σ_L	1.2240	(.7838, 2.7490)
σ^2_{LS}	1.4177	(1.0153, 2.1189)	σ_{LS}	1.1907	(1.0076, 1.4557)
σ^2_W	.1860	(.1511, .2346)	σ_W	.4313	(.3888, .4843)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.125. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.126.

TABLE 7.125. ANALYSIS OF VARIANCE FOR LOG$_e$ BARIUM DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	179	511.123	--	--
Leachate Samples	9	175.481	--	--
Laboratories	17	201.744	11.867	13.6*
Residual	153	133.897	.875	--

* $P < .005$

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .67$, $\sigma_L = .38$, and $\sigma = .55$. These values are smaller than the corresponding estimates given in Table 7.126, which indicates that greater precision may be attainable.

TABLE 7.126. VARIANCE COMPONENT ESTIMATES FOR LOG$_e$ BARIUM DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.9742	(1.3574, 3.1355)	σ_R	1.4051	(1.1651, 1.7707)
σ^2_L	1.0992	(.5952, 2.6746)	σ_L	1.0484	(.7715, 1.6354)
σ^2*	.8750	(.7078, 1.1097)	σ**	.9354	(.8413, 1.0534)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Iron Data Base

Data were received from 28 of the 49 laboratories that agreed to perform the iron analysis. The analysis was performed in triplicate by 15 laboratories for all 10 leachate samples. A single value or an average value was reported by 11 laboratories. The remaining 2 laboratories reported an unequal number of replicates.

No values were reported as detection limits (i.e., < value) for this parameter and no 0 mg/ℓ concentration levels were reported.

TABLE 7.127. SUMMARY OF ANALYTICAL RESULTS FOR IRON DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	227	139	386	226	5.8	47.5
B	337	48	563	345	24.9	126
C	279	4.4	453	300	9.78	81.2
D	754	285	1063	762	24.8	144
E	161	63	290	170	4.4	49.2
F	172	74	301	183	4.9	52.2
G	283	32	565	307	23.4	143
H	337	82.7	564	377	8.21	102
I	43.7	12	255	40.3	2.17	43.4
J	7.67	3	48	4.8	.506	9.44

*All entries in mg/ℓ.

A summary of the analytical results for the 10 leachate samples is given in Table 7.127. The average iron concentration of the samples ranged from 7.67 to 754 mg/ℓ, with the highest value generally 10 times larger than the lowest value for any particular leachate sample.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.83. A regression equation was calculated to be $\sigma = .0347\ \mu + 1.58$ with an R^2 value of 59%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .844 \log \mu - 1.06$ with an R^2 value of 87%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.57, 1.11), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within laboratory variance. Although the square root transformation was indicated to stabilize the between laboratory variance, the use of a logarithmic transformation may be adequate. The logarithmic transformed data were used in the statistical analysis of this parameter.

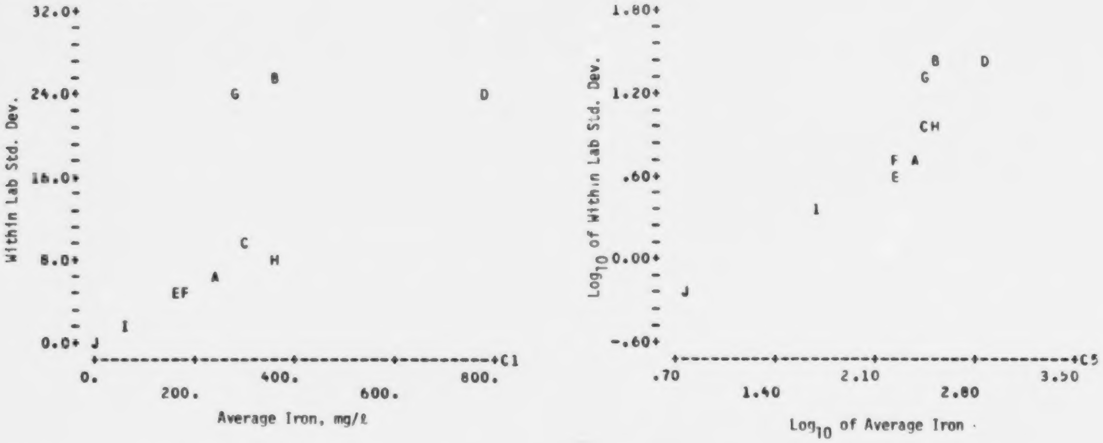

Figure 7.83. Relationship of the within laboratory standard deviation to the iron concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.84. A regression equation was calculated to be $\sigma = .183\ \mu + 32.1$ with an R^2 value of 66%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .587 \log \mu + .503$ with an R^2 value of 86%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.40, .78), which suggests that a square root transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

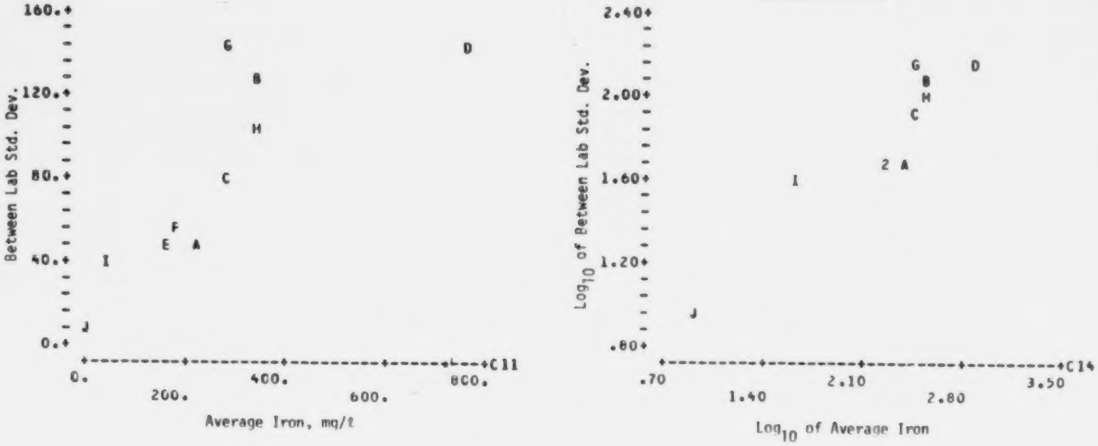

Figure 7.84. Relationship of the between laboratory standard deviation to the iron concentration level.

The ordered laboratory averages for the iron data plotted against the quantiles from a normal distribution are shown in Figure 28.3 for the ten leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 28.4 . The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 28.2.

TABLE 7.128. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average	Std. dev.
	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	90	95	87	89	92	92	96	81	43	42	81	21
Transformed	95	76	39	75	87	86	85	69	85	65	76	16

For the original data it appears that the distribution of the laboratory averages has a lighter lower tail and a heavier upper tail than the lower and upper tails of a normal distribution. The distribution of the $\log_e$ transformed data appears less similar to a normal distribution than the distribution of the original data, (i.e. closer to a straight line). This observation is supported by the lower R^2 values for 7 of the ten leachate samples, and the lower average R^2 for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data. Perhaps these data should be reanalyzed by converting the reported results into percentages of the sample average concentrations.

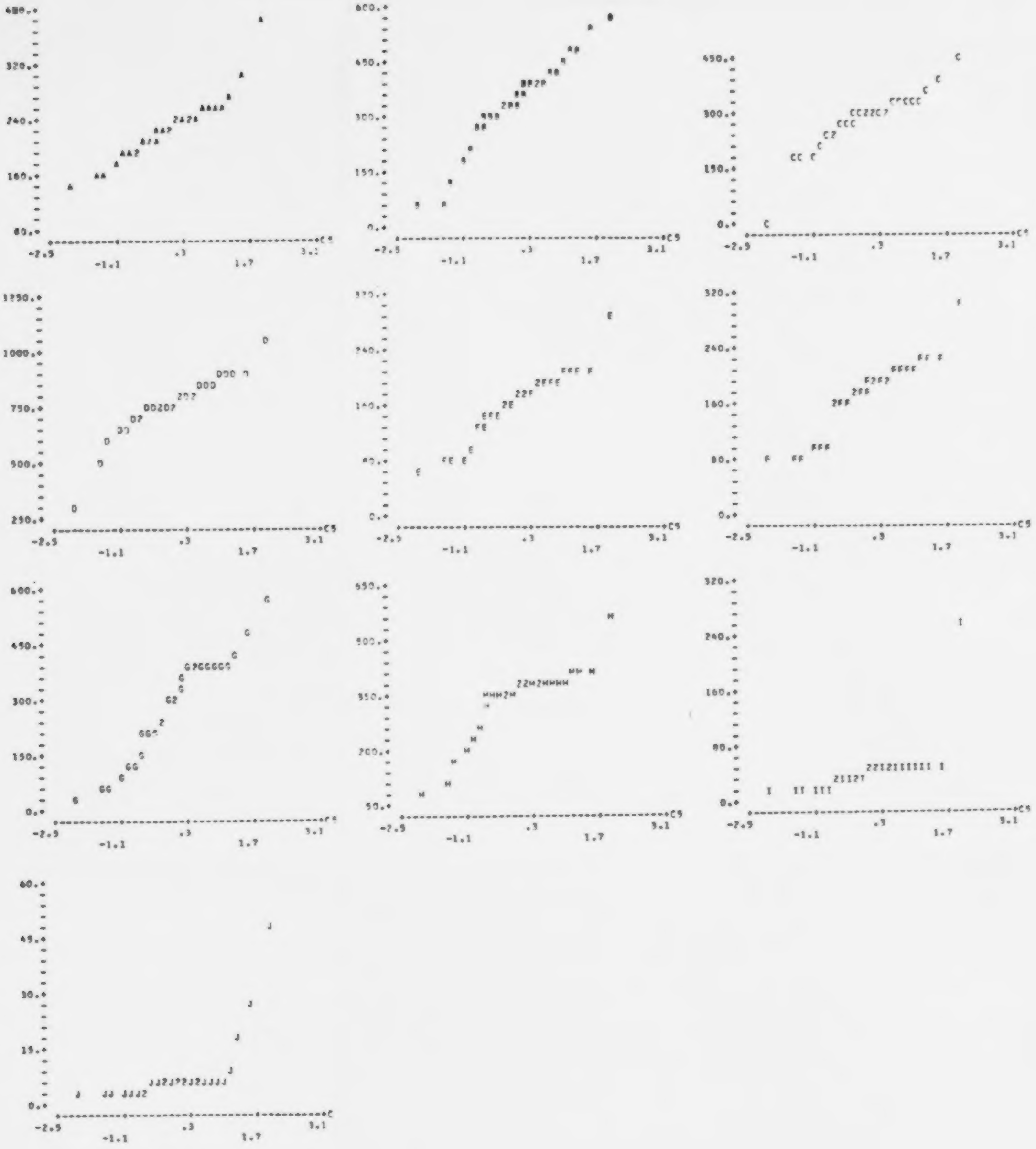

Figure 7.85. Ordered laboratory averages for iron data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

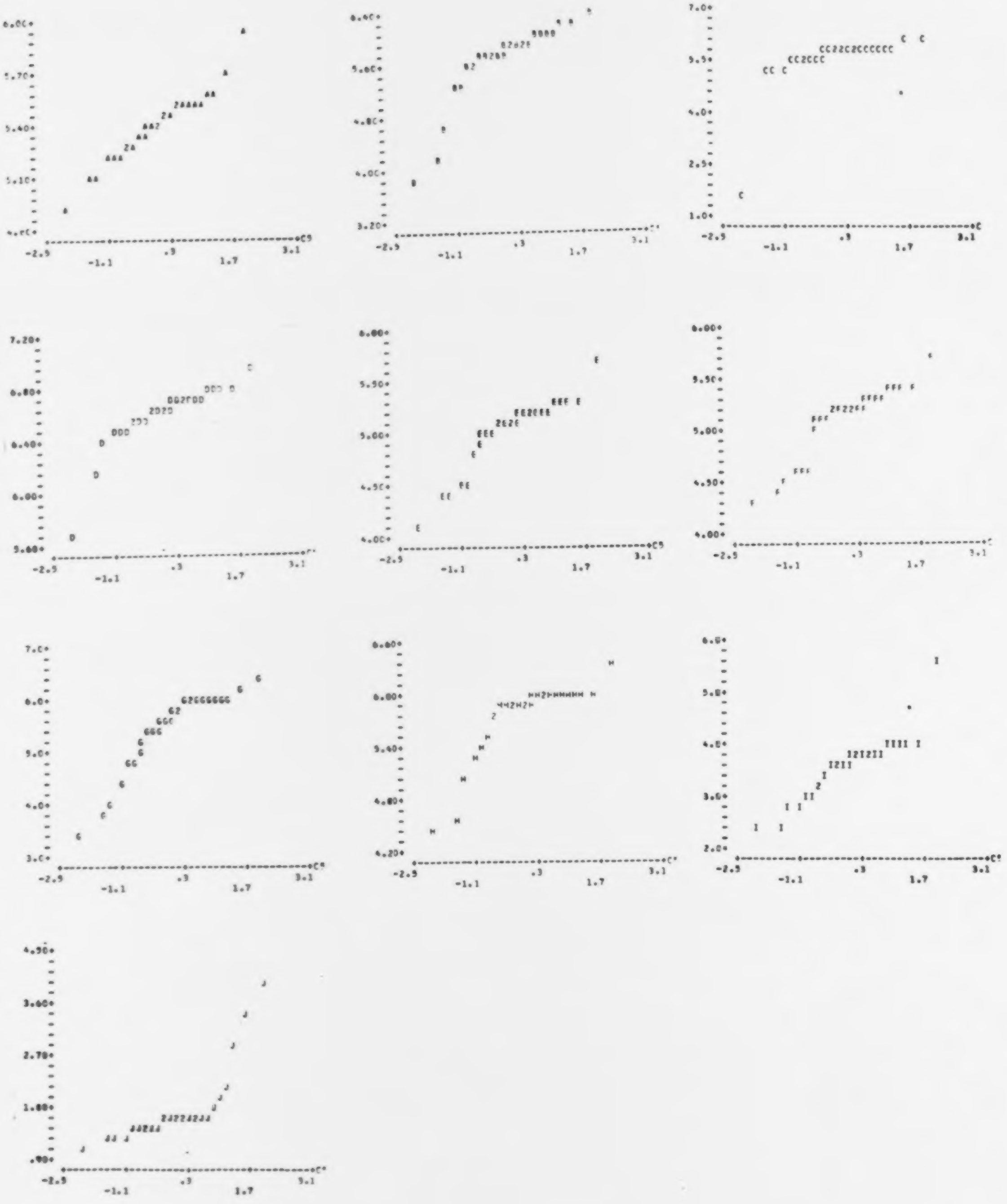

Figure 7.86. Ordered laboratory averages for $\log_e$ transformed iron data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed iron data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

TABLE 7.129. ANALYSIS OF VARIANCE FOR LOG_e IRON DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	449	861.22704	--	--
Leachate Samples	9	784.37822	--	--
Laboratories	14	28.38085	2.02720	5.36*
Lab x Sample	126	47.62071	.37794	134*
Residual	300	.84726	.00282	--

* $P < .005$

The data from 15 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.129. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.130.

TABLE 7.130. VARIANCE COMPONENT ESTIMATES FOR LOG_e IRON DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.1828	(.1365, .2576)	σ_R	.4276	(.3695, .5075)
σ^2_{LPLS}	.1800	(.1340, .2546)	σ_{LPLS}	.4243	(.3661, .5046)
σ^2_L	.0550	(.0262, .1798)	σ_L	.2345	(.1619, .4240)
σ^2_{LS}	.1250	(.0989, .1631)	σ_{LS}	.3536	(.3146, .4038)
σ^2_W	.0028	(.0024, .0033)	σ_W	.0531	(.0492, .0577)

TABLE 7.131. ANALYSIS OF VARIANCE FOR LOG_e IRON DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	279	549.316	--	--
Leachate Samples	9	473.097	--	--
Laboratories	27	26.764	.991	4.86*
Residual	243	49.456	.204	--

* $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.131. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.132.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .29$, $\sigma_L = .16$, and $\sigma = .24$. These values are smaller than the corresponding estimates given in Table 7.132, which indicates that greater precision may be attainable.

TABLE 7.132. VARIANCE COMPONENT ESTIMATES FOR LOG_e IRON DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.2827	(.2296, .3568)	σ_R	.5317	(.4791, .5973)
σ^2_L	.0787	(.0443, .1772)	σ_L	.2805	(.2104, .4210)
σ^2*	.2040	(.1721, .2458)	σ**	.4517	(.4148, .4957)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Zinc Data Base

Data were received from 29 of the 49 laboratories that agreed to perform the zinc analysis. The analysis was performed in triplicate by 15 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 10 laboratories. The remaining 3 laboratories reported an unequal number of replicates.

A summary of the analytical results for the 10 leachate samples is given in Table 7.133. The average zinc concentration of the samples ranged from 2.48 to 68.3 mg/ℓ, with the highest value generally 400 times larger than the lowest value for any particular leachate sample.

TABLE 7.133. SUMMARY OF ANALYTICAL RESULTS FOR ZINC DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	68.3	13.7	298	61.4	2.85	46.7
B	8.73	0.0	105	4.0	.565	19
C	37.8	.96	126	37.2	.993	20.5
D	4.4	.267	82.5	.787	.61	15.3
E	5.41	.433	71.7	2.43	2.15	13
F	4.67	.1	85	.5	.634	16.1
G	3.74	.16	57	1.03	1.92	10.7
H	8.09	0.0	204	.66	2.18	37.7
I	2.48	0.0	60.3	.08	.754	11.2
J	4.12	.08	69	1.19	.687	12.7

*All entries in mg/ℓ.

Two values ranging from .01 to .02 mg/ℓ were reported as detection limits (i.e., < value) by 2 laboratories. A complete listing of these values is given in Table A-9 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Nine mg/ℓ concentration levels were reported for leachate samples B, H, and I with frequency 3, 3, and 3, respectively.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.87. A regression equation was calculated to be $\sigma = .0207\ \mu + .977$ with an R^2 value of 30%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .309 \log \mu - .267$ with an R^2 value of 21%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (-.18, .80), which suggests that a square root or no transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

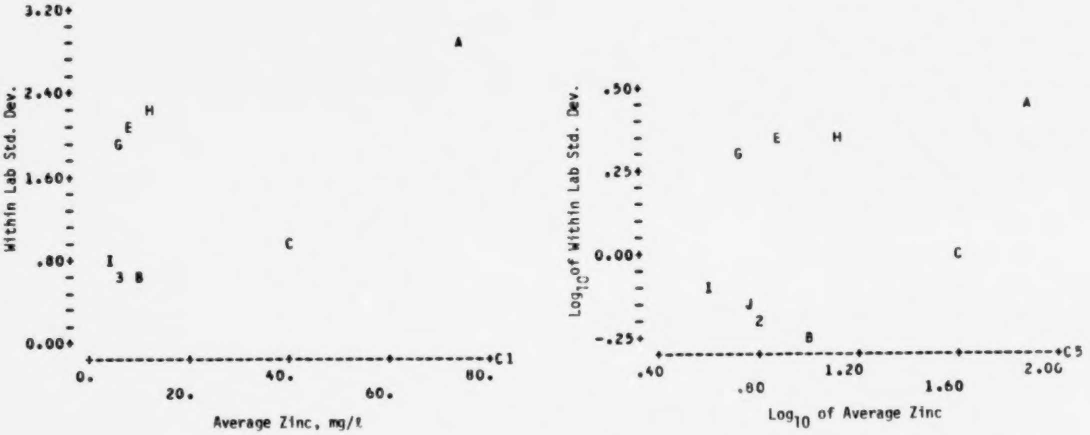

Figure 7.87. Relationship of the within laboratory standard deviation to the zinc concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.88. A regression equation was calculated to be $\sigma = .425\ \mu + 14.0$ with an R^2 value of 57%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .365 \log \mu + .928$ with an R^2 value of 61%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.12, .61), which suggests that a square root transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

Although the square root transformation was indicated to stabilize the within and between laboratory variances, the appearance of the graphs and low R^2 values make the choice of a transformation uncertain. The natural logarithms of the reported concentration level were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, .0025 was added to all zero values. These transformed data were used in the statistical analysis of this parameter.

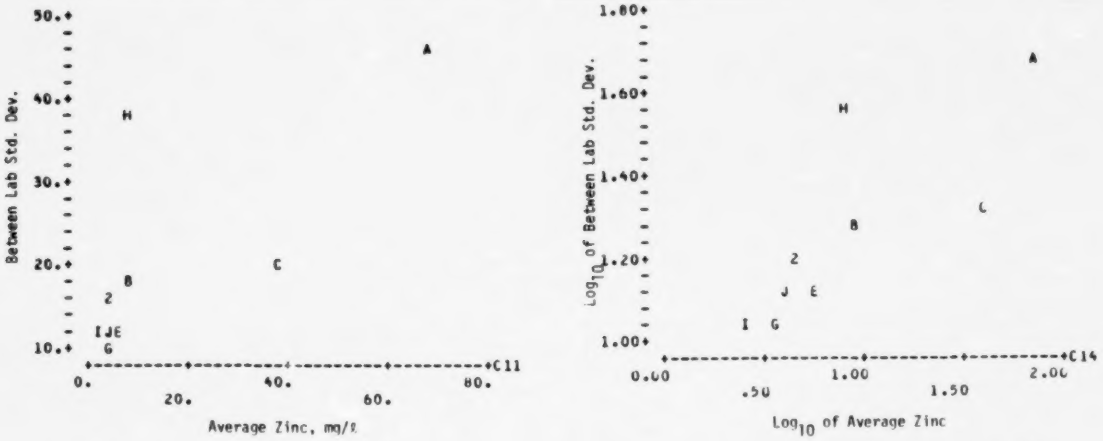

Figure 7.88. Relationship of the between laboratory standard deviation to the zinc concentration level.

The ordered laboratory averages for the zinc data plotted against the quantiles from a normal distribution are shown in Figure 7.89 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.90. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.134

TABLE 7.134. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample A	B	C	D	E	F	G	H	I	J	Average R^2	Std. dev. of R^2
Original	40	34	68	24	28	28	31	18	20	25	32	14
Transformed	65	74	59	63	77	69	92	71	84	62	72	10

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data, (i.e. closer to a straight line). This observation is supported by the higher R^2 values for 9 of the 10 leachate samples, the greater average R^2 , and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

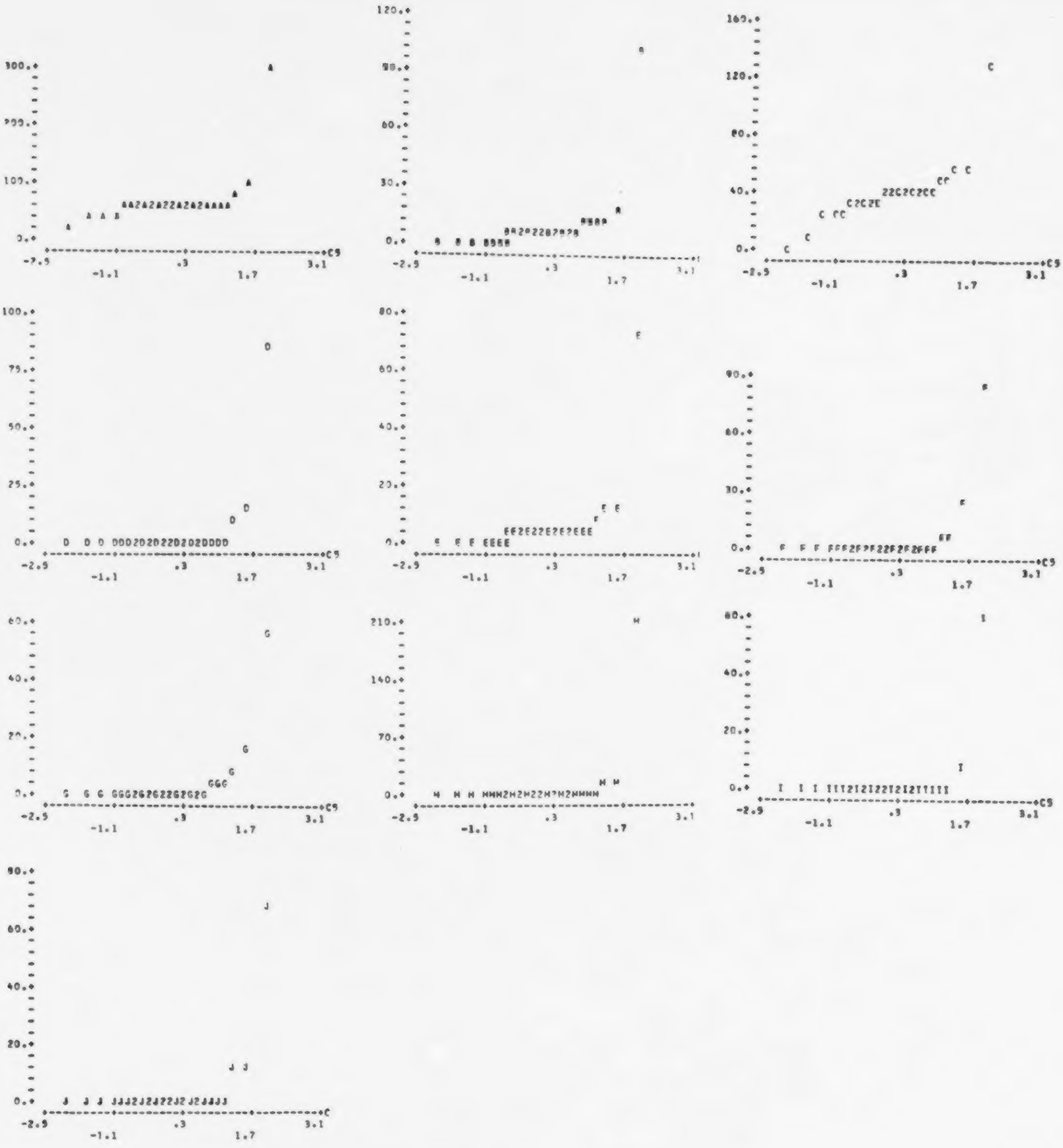

Figure 7.89. Ordered laboratory averages for zinc data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

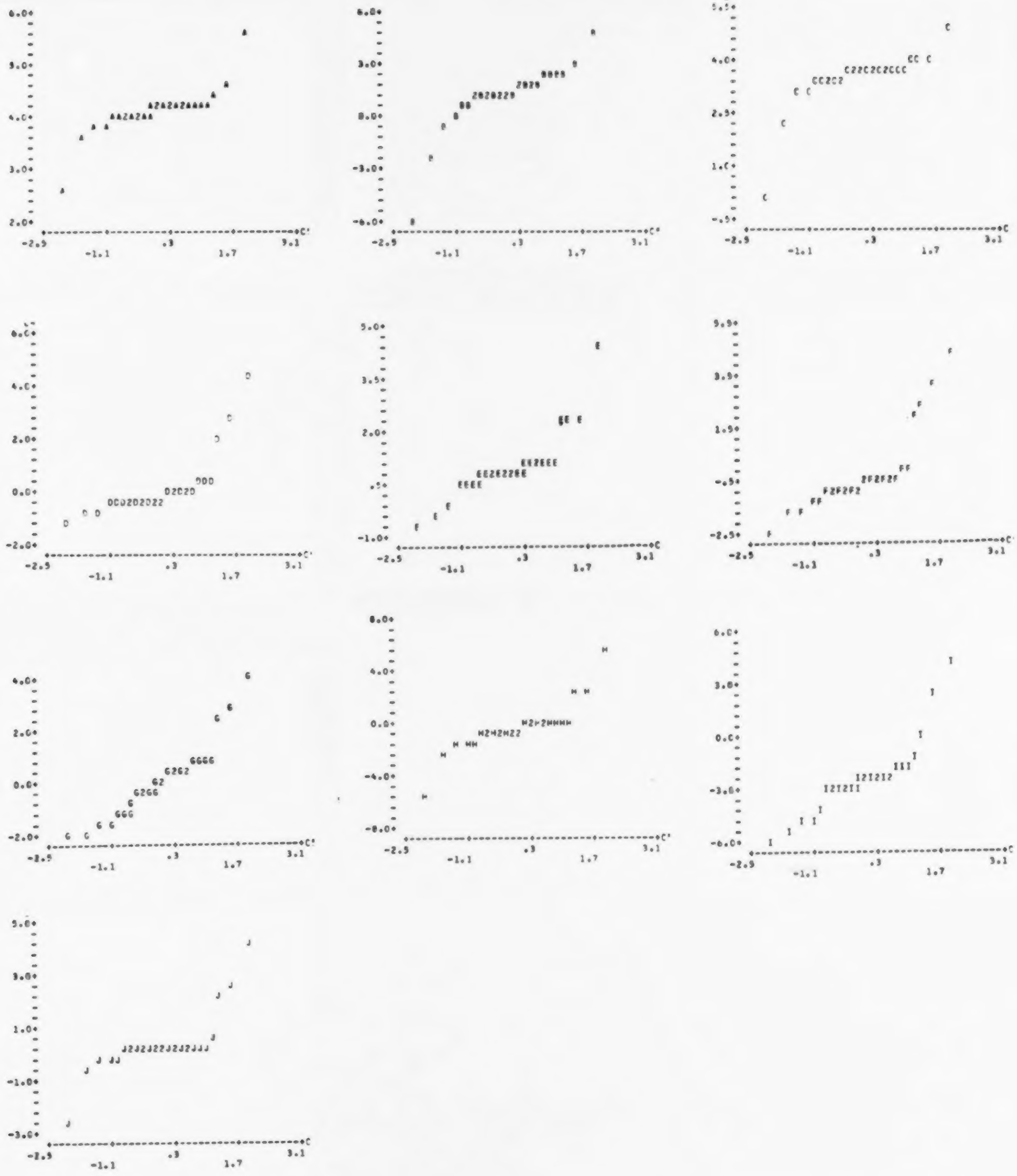

Figure 7.90. Ordered laboratory averages for $\log_e$ transformed zinc data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate sample A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed zinc data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

TABLE 7.135. ANALYSIS OF VARIANCE FOR LOG_e ZINC DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	449	2047.9276	--	--
Leachate Samples	9	1444.9684	--	--
Laboratories	14	358.6068	25.6148	13.4*
Lab x Sample	126	241.1757	1.9141	181 *
Residual	300	3.1767	.0106	--

* $P < .005$

The data from 15 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.135. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.136.

TABLE 7.136. VARIANCE COMPONENT ESTIMATES FOR LOG_e ZINC DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.4351	(.9566, 2.3907)	σ_R	1.1980	(.9781, 1.5462)
σ^2_{LPLS}	1.4245	(.9470, 2.3830)	σ_{LPLS}	1.1935	(.9732, 1.5437)
σ^2_L	.7900	(.4058, 2.1562)	σ_L	.8888	(.6370, 1.4684)
σ^2_{LS}	.6345	(.5023, .8271)	σ_{LS}	.7966	(.7087, .9094)
σ^2_W	.0106	(.0091, .0125)	σ_W	.1030	(.0953, .1119)

TABLE 7.137. ANALYSIS OF VARIANCE FOR LOG_e ZINC DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	289	1460.693	--	--
Leachate Samples	9	946.650	105.183	--
Laboratories	28	319.889	11.425	14.8*
Residual	252	194.154	.770	--

* $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.137. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.138.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .41$, $\sigma_L = .18$, and $\sigma = .37$. These values are considerably smaller than the corresponding estimates given in Table 7.138, which indicates that greater precision may be attainable.

TABLE 7.138. VARIANCE COMPONENT ESTIMATES FOR LOG_e ZINC DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.8355	(1.3505, 2.6398)	σ_R	1.3548	(1.1621, 1.6248)
σ^2_L	1.0655	(.6514, 2.0517)	σ_L	1.0322	(.8071, 1.4324)
σ^2*	.7700	(.6514, .9244)	σ**	.8775	(.8071, .9614)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Lead Data Base

Data were received from 27 of the 49 laboratories that agreed to perform the lead analysis. The analysis was performed in triplicate by 12 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 11 laboratories. The remaining 3 laboratories reported an unequal number of replicates.

A summary of the analytical results for the 10 leachate samples is given in Table 7.139. The average lead concentration of the samples ranged from .0471 to .842 mg/ℓ, with the highest value generally 75 times larger than the lowest value for any particular leachate sample.

TABLE 7.139. SUMMARY OF ANALYTICAL RESULTS FOR LEAD DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	.842	.212	2.91	.782	.0864	.601
B	.175	.006	.533	.18	.0661	.114
C	.457	.025	2.13	.44	.029	.379
D	.19	.011	.697	.2	.0173	.125
E	.308	.0903	1.27	.3	.0621	.218
F	.317	.025	1.51	.3	.0204	.262
G	.0945	.005	.453	.05	.021	.0978
H	.0471	.00333	.25	.025	.00578	.0579
I	.0641	.00333	.347	.04	.0064	.0754
J	.058	0.0	.338	.025	.16	.0818

*All entries in mg/ℓ.

Eighty-one values ranging from .02 to .5 mg/ℓ were reported as detection limits (i.e., < value) by 8 laboratories. The difference in magnitude for these values is comparatively large. A complete listing of these values is given in Table A-10 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. One mg/ℓ concentration level for leachate sample J was reported.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.91. A regression equation was calculated to be $\sigma = .0291\ \mu + .0391$ with an R^2 value of 3%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .539 \log \mu - 1.16$ with an R^2 value of 19%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (-.38, 1.46), which suggests that a square root or logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

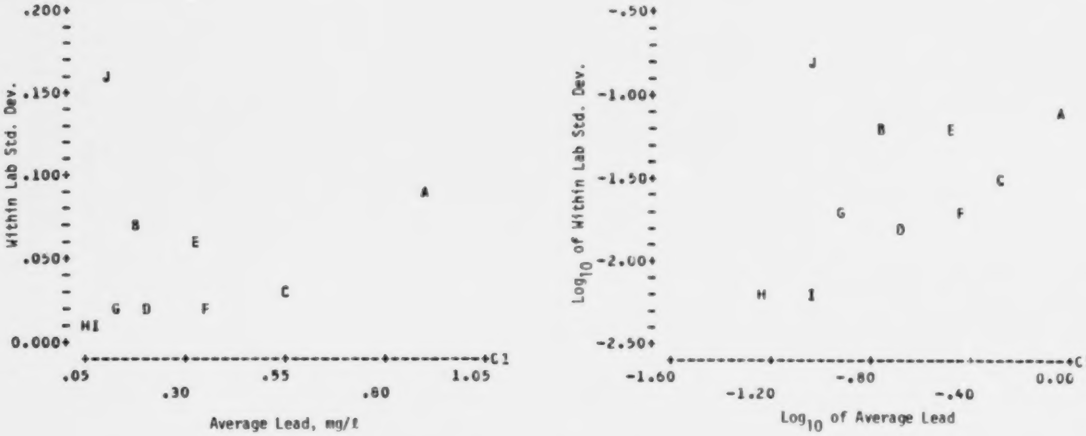

Figure 7.91. Relationship of the within laboratory standard deviation to the lead concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.92. A regression equation was calculated to be $\sigma = .697\ \mu + .0233$ with an R^2 value of 98%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .771 \log \mu - .226$ with an R^2 value of 95%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.62, .92), which suggests that a square root or logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

Although the square root transformation was indicated to stabilize the within laboratory variance, the appearance of the graphs and low R^2 value makes the choice of a transformation uncertain. The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, .0008 was added to all zero values. These transformed data were used in the statistical analysis of this parameter.

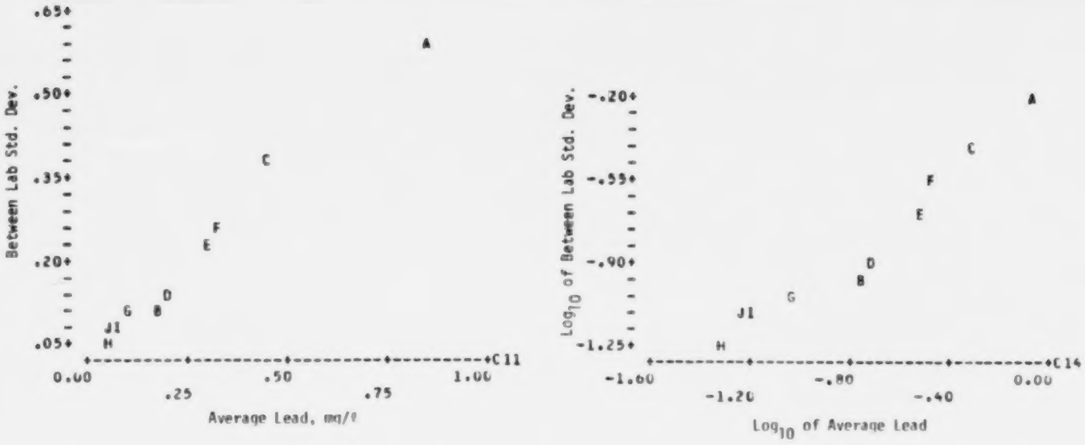

Figure 7.92. Relationship of the between laboratory standard deviation to the lead concentration level.

The ordered laboratory averages for the lead data plotted against the quantiles from a normal distribution are shown in Figure 7.93 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.94. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.140.

TABLE 7.140. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average	Std. dev.
	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	83	91	62	74	61	56	73	71	66	68	71	11
Transformed	93	81	85	83	91	82	96	97	98	97	90	7

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for 9 of the 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in some of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

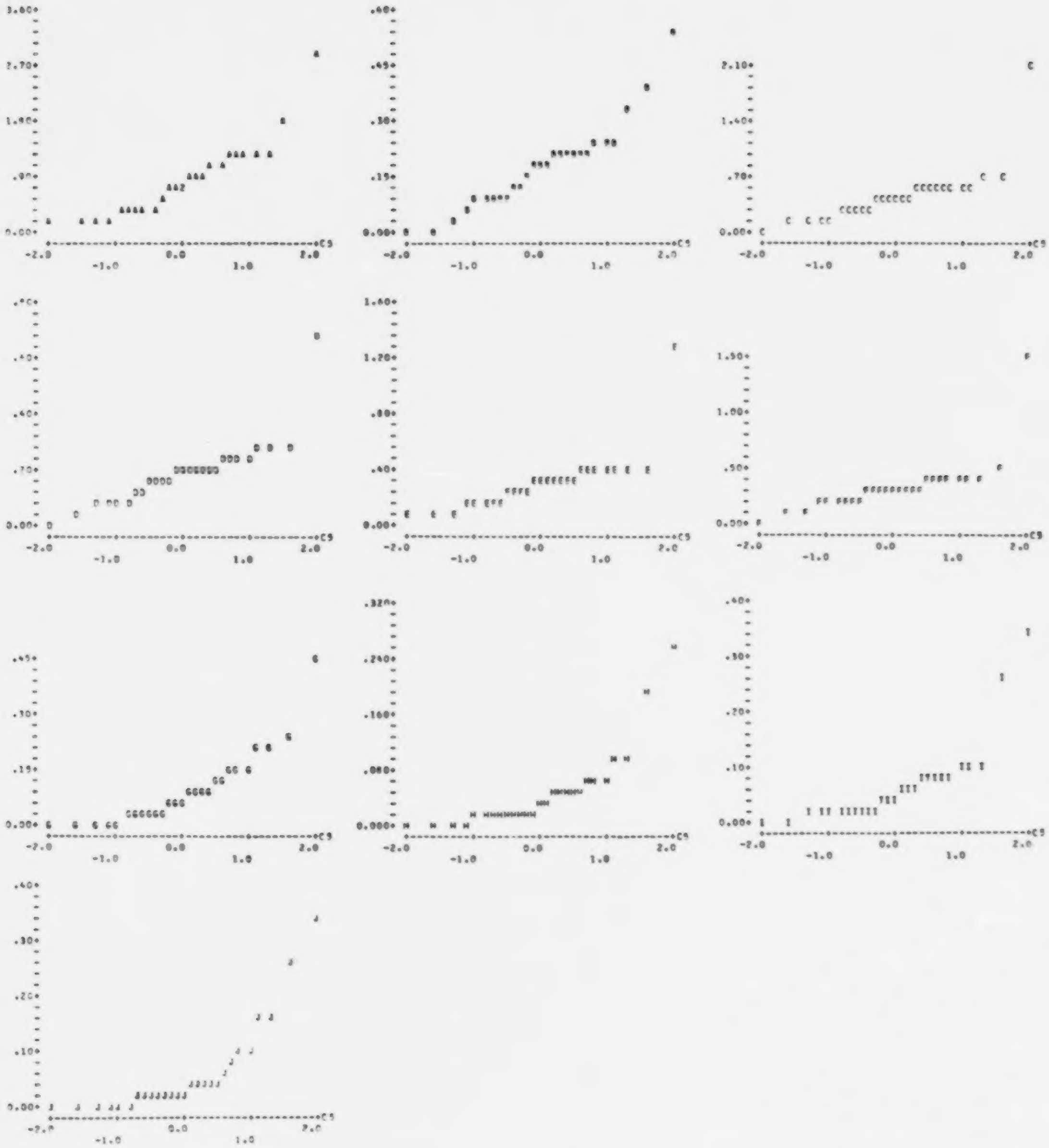

Figure 7.93. Ordered laboratory averages for lead data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

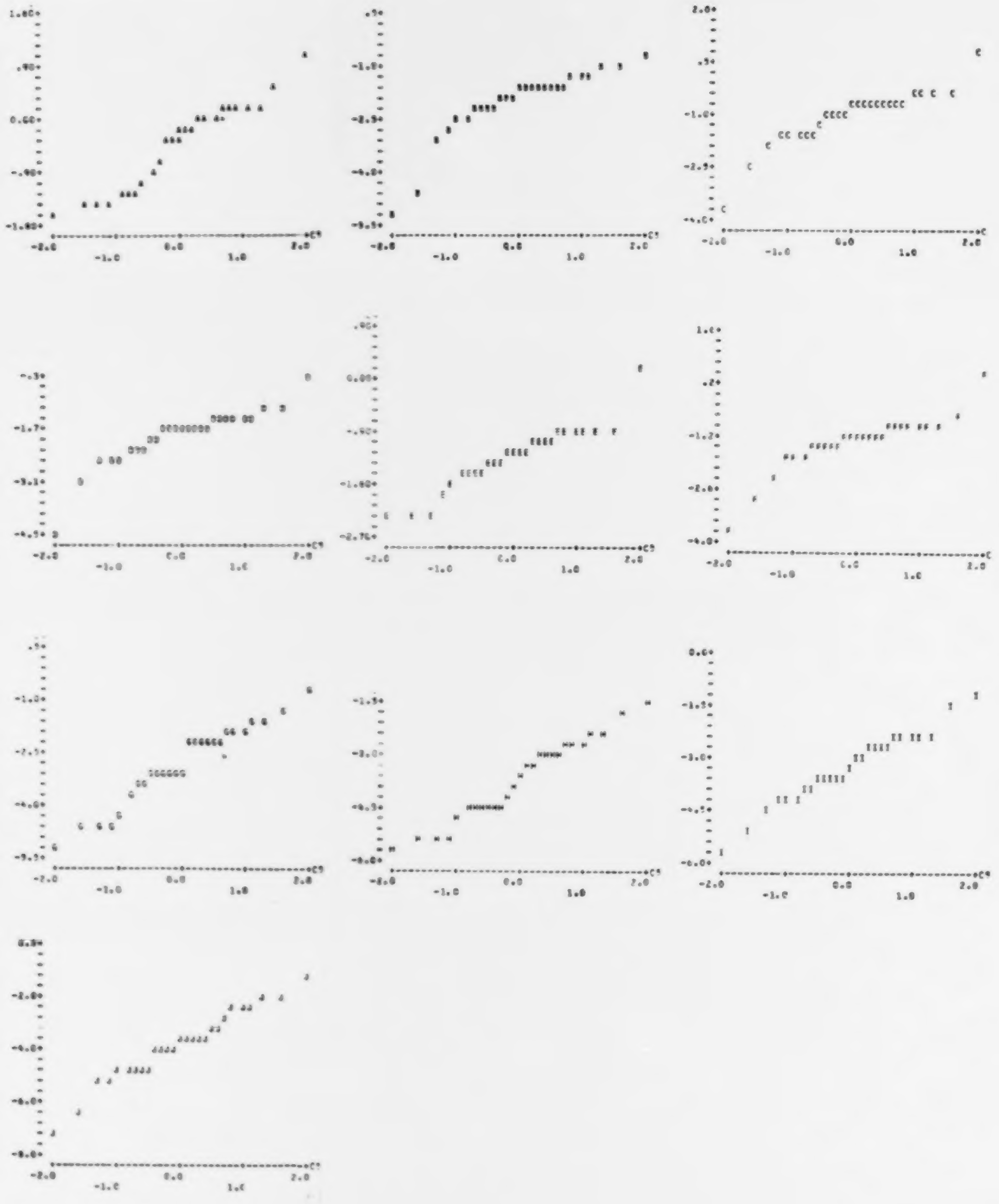

Figure 7.94. Ordered laboratory averages for $\log_e$ transformed lead data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed lead data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 12 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.141. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.142.

TABLE 7.141. ANALYSIS OF VARIANCE FOR LOG_e LEAD DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	359	797.5375	--	--
Leachate Samples	9	407.15	--	--
Laboratories	11	234.9374	21.3579	15.9*
Lab x Sample	99	132.6877	1.3403	14.1*
Residual	240	22.7624	.0948	--

* $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.143. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.144.

TABLE 7.142. VARIANCE COMPONENT ESTIMATES FOR LOG$_E$ LEAD DATA BASED ON LABORATORIES REPORTING THREE REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.1772	(.7461, 2.1296)	σ_R	1.0850	(.8638, 1.4593)
σ^2_{LPLS}	1.0824	(.6630, 2.0773)	σ_{LPLS}	1.0404	(.8143, 1.4413)
σ^2_L	.6673	(.3223, 2.1095)	σ_L	.8169	(.5677, 1.4524)
σ^2_{LS}	.4152	(.3141, .5745)	σ_{LS}	.6443	(.5605, .7580)
σ^2_W	.0948	(.0799, .1143)	σ_W	.3079	(.2826, .3381)

TABLE 7.143. ANALYSIS OF VARIANCE FOR LOG$_e$ LEAD DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	269	578.700	--	--
Leachate Samples	9	338.156	--	--
Laboratories	26	122.161	4.699	9.29*
Residual	234	118.383	.506	--

* $P < .005$

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .79$, $\sigma_L = .51$, and $\sigma = .60$. These values are smaller than the corresponding estimates given in Table 7.144.

Chromium Data Base

Data were received from 28 of the 49 laboratories that agreed to perform the chromium analysis. The analysis was performed in triplicate by 14 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 11 laboratories The remaining 2 laboratories reported an unequal number of replicates.

TABLE 7.144. VARIANCE COMPONENT ESTIMATES FOR LOG_e LEAD DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	.9253	(.7062, 1.2656)	σ_R	.9619	(.8403, 1.1250)
σ^2_L	.4193	(.2472, .8623)	σ_L	.6475	(.4972, .9286)
σ^2*	.5060	(.4255, .6118)	σ**	.7113	(.6523, .7822)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Eighty-four values ranging from .005 to .1 mg/ℓ were reported as detection limits (i.e., < value) by 8 laboratories. The difference in magnitude for these values is comparatively large. A complete listing of these values is given in Table A-11 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Fourty-six 0 mg/ℓ concentration levels were reported for leachate samples A, B, D, E, F, G, H, I, and J with frequency 3, 4, 3, 3, 5, 5, 5, 8, and 10, respectively. Five laboratories reported one or more zero concentration levels.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.95. A regression equation was calculated to be $\sigma = .278\ \mu - .05$ with an R^2 value of 66%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.23 \log \mu - .897$ with an R^2 value of 96%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (1.02, 1.45), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

A summary of the analytical results for the 10 leachate samples is given in Table 7.145 . The average chromium concentration of the samples ranged from .08 to 4.59 mg/ℓ, with the highest value generally 1000 times larger than the lowest value for any particular leachate sample.

TABLE 7.145. SUMMARY OF ANALYTICAL RESULTS FOR CHROMIUM DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	.48	0	1.77	.41	.033	.324
B	.15	0	1.42	.0682	.013	.293
C	.418	0.01	1.69	.302	.054	.337
D	.158	0	1.75	.05	.01	.385
E	.228	0	0.943	.18	.015	.196
F	.08	0	0.697	.0302	.007	.145
G	.096	0	1.23	.034	.013	.233
H	4.7	0	129	.02	1.75	24.4
I	4.41	0	123	.02	.635	23.1
J	4.59	0	120	.02	3.66	22.6

*All entries in mg/ℓ.

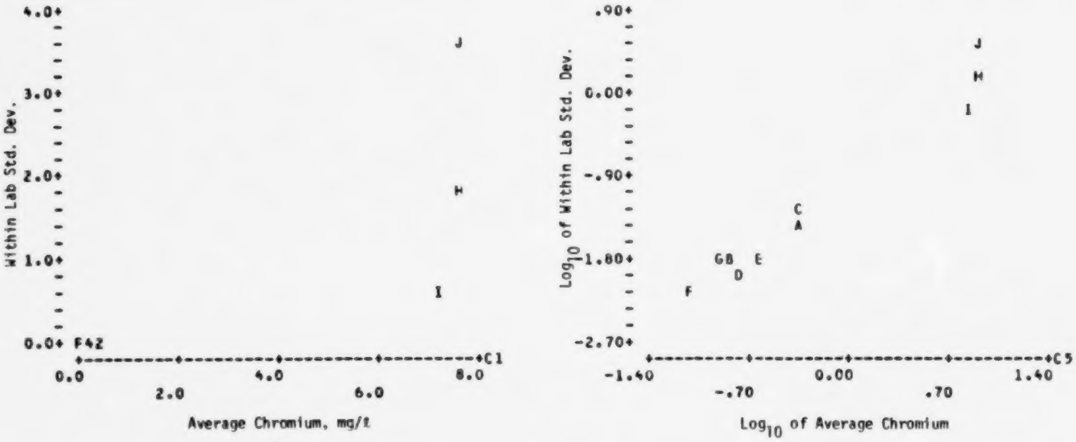

Figure 7.95. Relationship of the within laboratory standard deviation to the chromium concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.96. A regression equation was calculated to be $\sigma = 5.31\ \mu - .921$ with an R^2 value of 100%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = 1.28 \log \mu + .399$ with an R^2 value of 92%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.97, 1.59), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, .0005 was added to all zero values. These transformed data were used in the statistical analysis of this parameter.

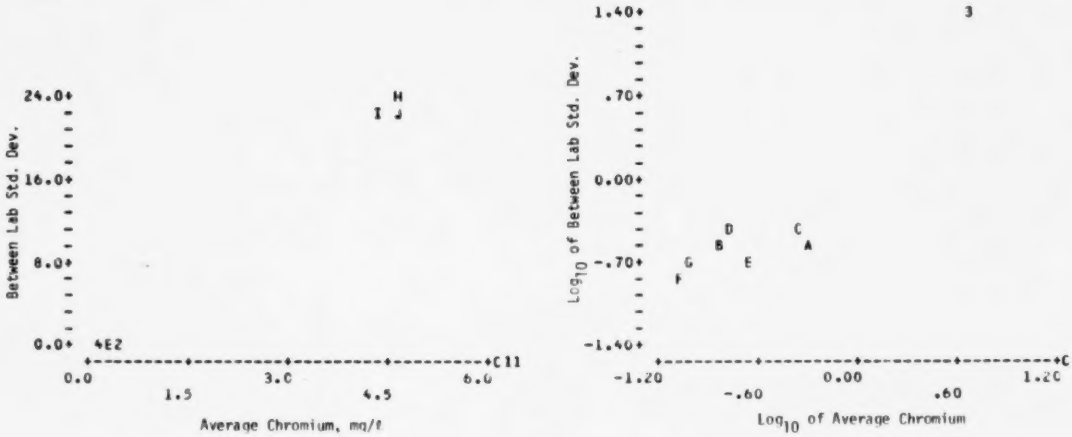

Figure 7.96. Relationship of the between laboratory standard deviation to the chromium concentration level.

The ordered laboratory averages for the chromium data plotted against the quantiles from a normal distribution are shown in Figure 31.3 for the ten leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 31.4 . The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 31.2

TABLE 7.146. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average R^2	Std. dev. of R^2
	A	B	C	D	E	F	G	H	I	J		
Original	71	44	69	36	74	52	34	17	17	19	43	23
Transformed	45	88	72	83	65	96	93	79	81	78	78	15

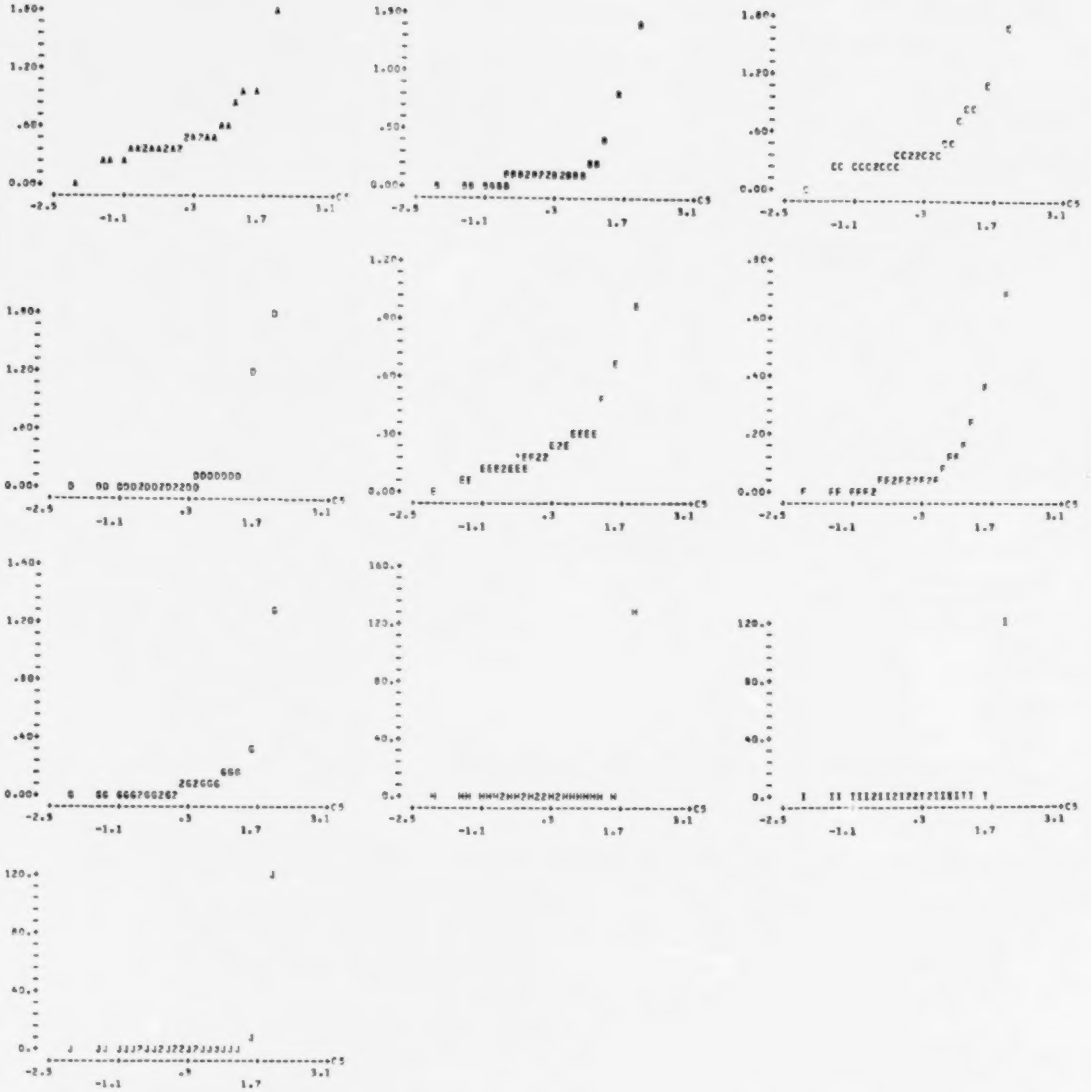

Figure 7.97. Ordered laboratory averages for chromium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J respectively.

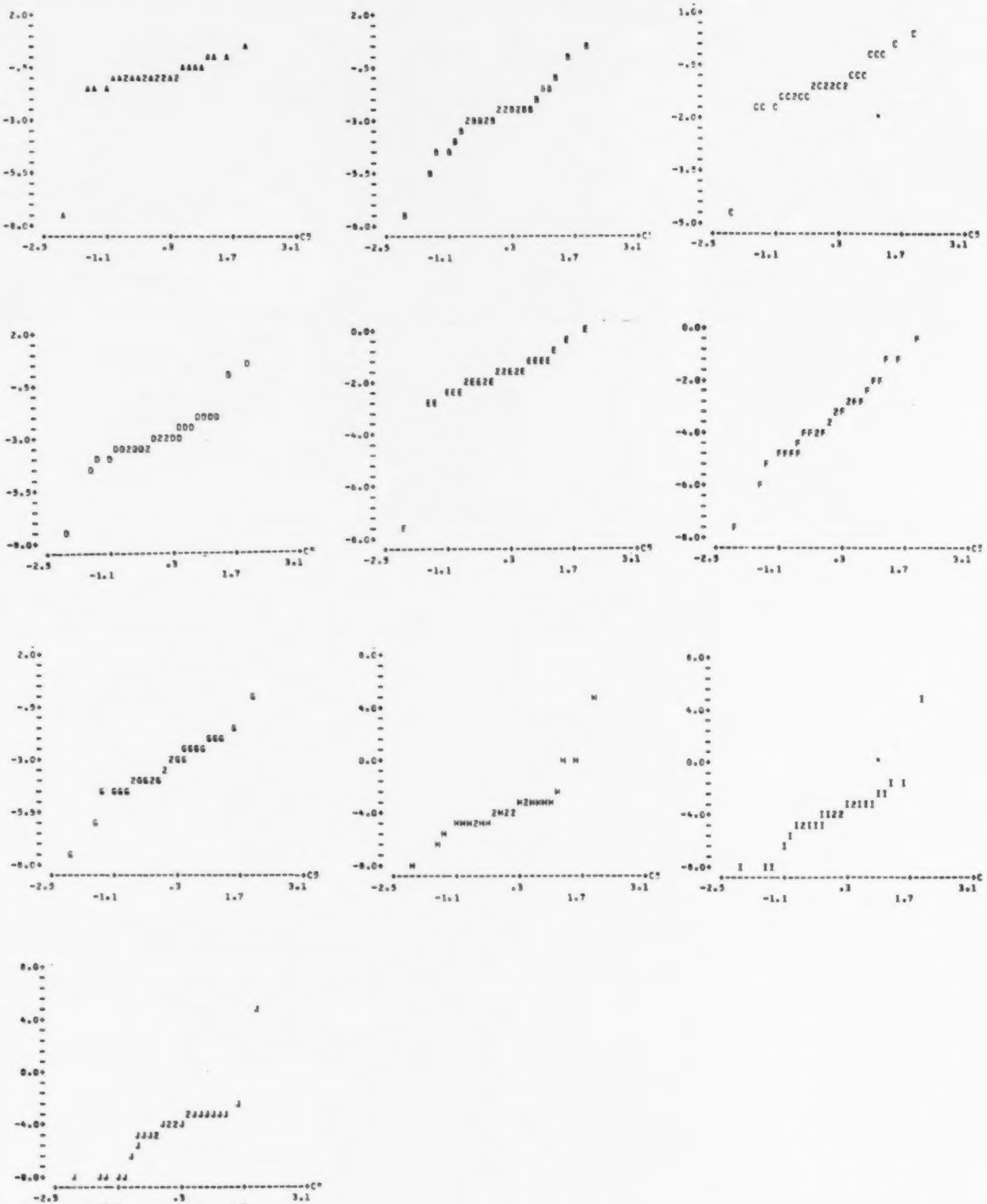

Figure 7.98. Ordered laboratory averages for $\log_e$ transformed chromium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J respectively.

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for 9 of the 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed chromium data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 14 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.147. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the lao-ratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.148.

TABLE 7.147. ANALYSIS OF VARIANCE FOR LOG_e CHROMIUM DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	419	1731.515	--	--
Leachate Samples	9	538.494	59.833	--
Laboratories	13	832.017	64.001	31.6*
Lab x Sample	117	237.326	2.028	4.59*
Residual	280	123.679	.442	--

* $P < .005$

TABLE 7.148. VARIANCE COMPONENT ESTIMATES FOR LOG_e CHROMIUM DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	3.0364	(1.8832, 5.7015)	σ_R	1.7425	(1.3723, 2.3878)
σ^2_{LPLS}	2.5944	(1.5007, 5.5298)	σ_{LPLS}	1.6107	(1.2250, 2.3516)
σ^2_L	2.0658	(1.0665, 5.5776)	σ_L	1.4373	(1.0327, 2.3617)
σ^2_{LS}	.5287	(.3896, .7588)	σ_{LS}	.7271	(.6242, .8711)
σ^2_W	.4420	(.3770, .5254)	σ_W	.6648	(.6140, .7249)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.149. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.150.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .70$, $\sigma_L = .46$, and $\sigma = .53$. These values are smaller than the corresponding estimates given in Table 7.150, which indicates that greater precision may be attainable.

TABLE 7.149. ANALYSIS OF VARIANCE FOR LOG_e CHROMIUM DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	279	1104.95	--	--
Leachate Samples	9	312.62	34.74	--
Laboratories	27	499.96	18.52	15.4*
Residual	243	292.38	1.20	--

* $P < .005$

TABLE 7.150. VARIANCE COMPONENT ESTIMATES FOR LOG_e CHROMIUM DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	2.9320	(2.1380, 4.2707)	σ_R	1.7123	(1.4622, 2.0666)
σ^2_L	1.7320	(1.0518, 3.3747)	σ_L	1.3161	(1.0256, 1.8370)
σ^2*	1.2000	(1.0122, 1.4456)	σ**	1.0954	(1.0061, 1.2023)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Cadmium Data Base

Data were received from 27 of the 48 laboratories that agreed to perform the cadmium analysis. The analysis was performed in triplicate by 14 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 10 laboratories. The remaining 2 laboratories reported an unequal number of replicates.

One hundred twenty-three values ranging from .0005 to .02 mg/ℓ were reported as detection limits (i.e., < value) by 13 laboratories. The difference in magnitude for these values is comparatively large. A complete listing of these values is given in Table A-12 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Forty-five 0 mg/ℓ concentration levels were reported for leachate samples A, B, C, D, E, F, G, H, I, and J with frequency 3, 3, 3, 4, 4, 4, 5, 5, 6, and 8, respectively. Five laboratories reported one or more zero concentration levels.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.99. A regression equation was calculated to be $\sigma = .357\ \mu + .0074$ with an R^2 value of 9%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .948 \log \mu - .587$ with an R^2 value of 53%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.22, 1.67), which suggests that a logarithm transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

A summary of the analytical results for the 10 leachate samples is given in Table 7.151 . The average cadmium concentration of the samples ranged from .008 to .13 mg/ℓ, with the highest value generally 500 times larger than the lowest value for any particular leachate sample.

TABLE 7.151. SUMMARY OF ANALYTICAL RESULTS FOR CADMIUM DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	.13	0	.36	.13	.0156	.0906
B	.043	0	.668	.01	.147	.128
C	.07	0	.4	.06	.0158	.078
D	.025	0	.08	.02	.0073	.0227
E	.033	0	.357	.015	.0054	.0691
F	.01	0	.04	.0093	.0042	.00987
G	.029	0	.5	.0073	.0165	.0949
H	.009	0	.0943	.005	.0027	.0184
I	.008	0	.05	.005	.0031	.0107
J	.049	0	1.0	.005	.0037	.194

*All entries in mg/ℓ

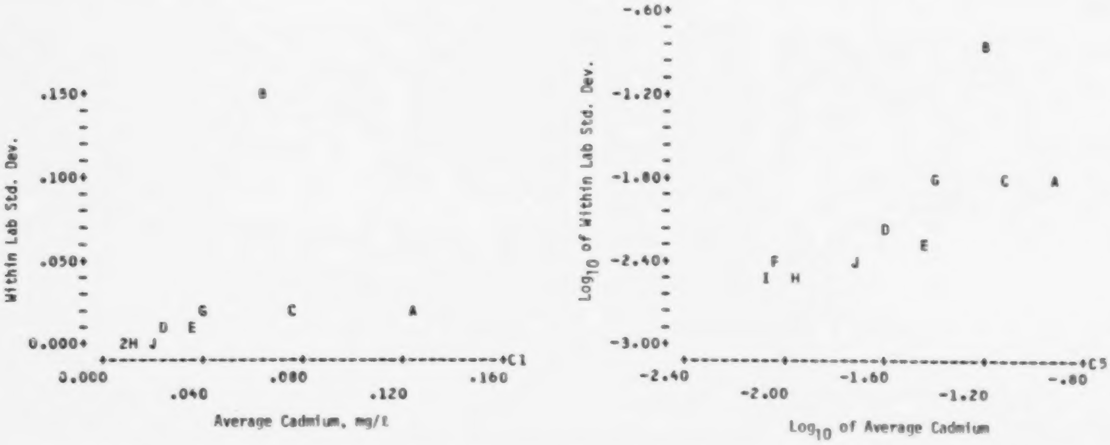

Figure 7.99. Relationship of the within laboratory standard deviation to the cadmium concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.100. A regression equation was calculated to be $\sigma = .739\ \mu + .0416$ with an R^2 value of 21%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .968 \log \mu + .168$ with an R^2 value of 69%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.43, 1.50), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

Although the logarithmic transformation was indicated to stabilize the within and between laboratory variance, the appearance of the graphs and low R^2 values makes the choice of a transformation uncertain. The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before appylying the transformation, .00001 was added to all zero values. These transformed data were used in the statistical analysis of this parameter.

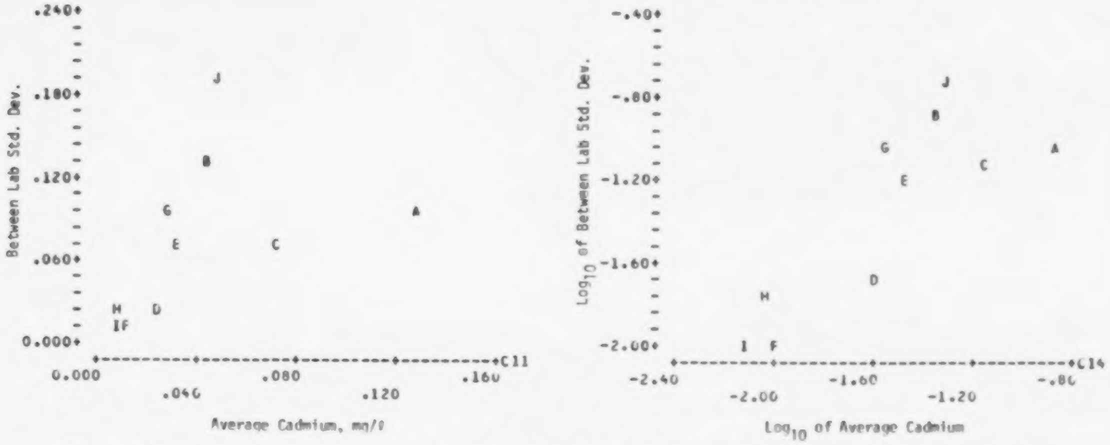

Figure 7.100. Relationship of the between laboratory standard deviation to the cadmium concentration level.

The ordered laboratory averages for the cadmium data plotted against the quantiles from a normal distribution are shown in Figure 7.101 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.102. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.152.

TABLE 7.152. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average R^2	Std. dev. of R^2
	A	B	C	D	E	F	G	H	I	J		
Original	96	29	64	80	38	86	26	45	66	24	55	27
Transformed	62	85	68	72	77	82	94	86	85	94	81	11

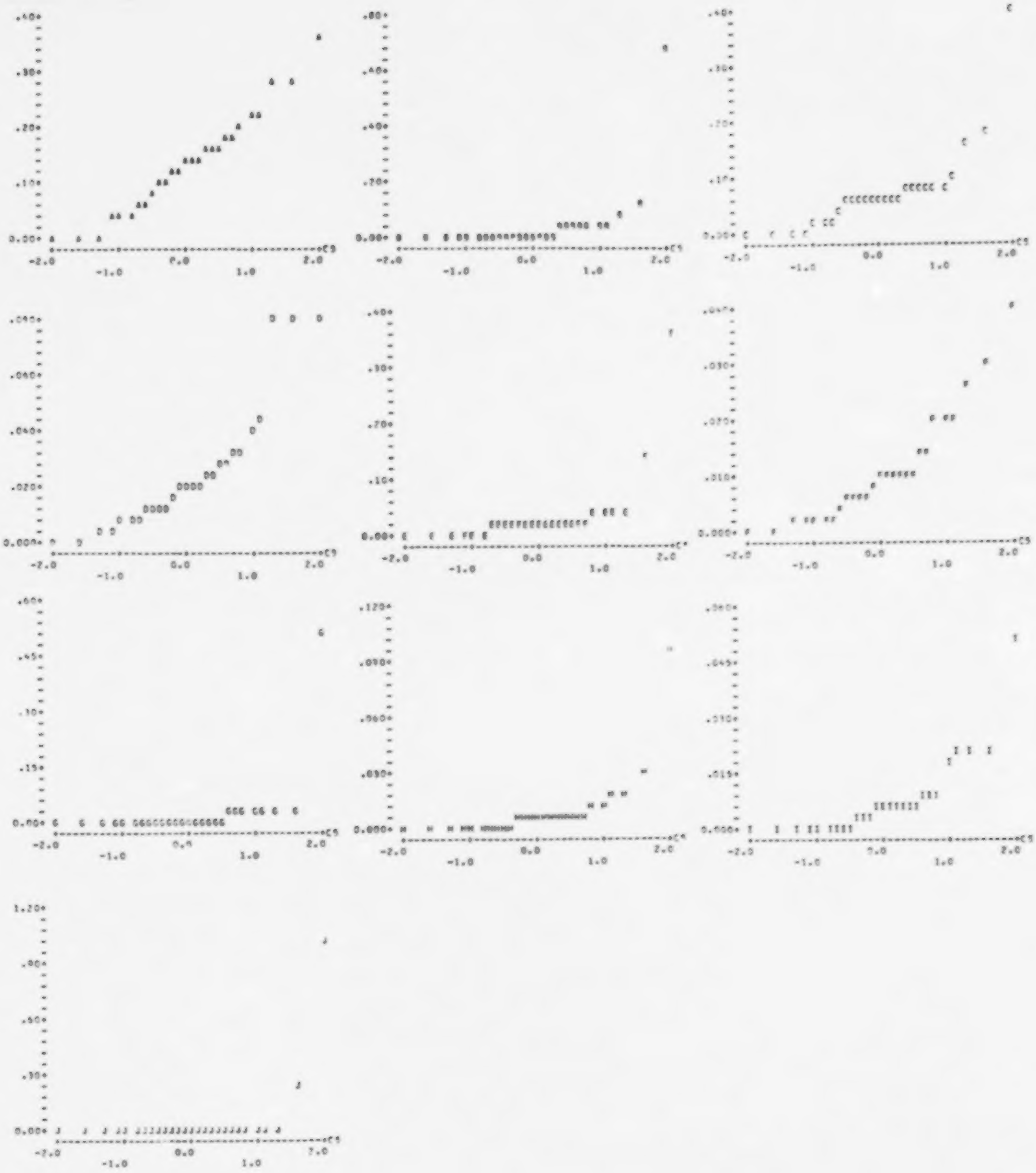

Figure 7.101. Ordered laboratory averages for cadmium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

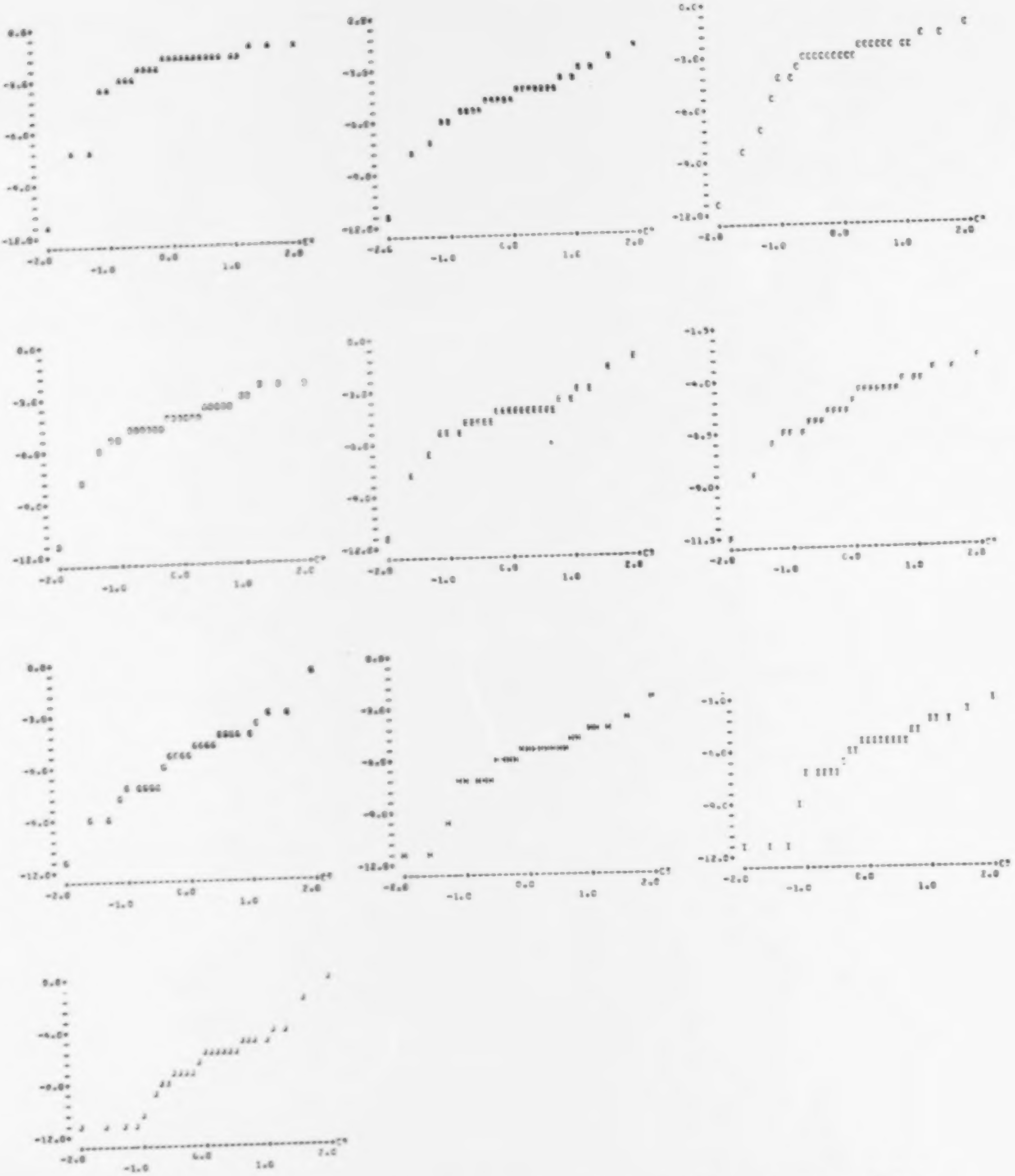

Figure 7.102. Ordered laboratory averages for $\log_e$ transformed cadmium data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). This observation is supported by the higher R^2 values for 7 of the 10 leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Several outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed cadmium data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 14 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.153. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.154.

TABLE 7.153. ANALYSIS OF VARIANCE FOR LOG_e CADMIUM DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	419	3084.45	--	--
Leachate Samples	9	465.21	51.69	--
Laboratories	13	2121.97	163.23	98.3*
Lab x Sample	117	194.26	1.66	1.54*
Residual	280	303.01	1.08	--

* $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.155. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.156.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = 1.0$, $\sigma_L = .76$, and $\sigma = .64$. These values are smaller than the corresponding estimates given in Table 7.156, which indicates that greater precision may be attainable.

TABLE 7.154. VARIANCE COMPONENT ESTIMATES FOR LOG_e CADMIUM DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	6.6590	(3.8707, 14.0658)	σ_R	2.5805	(1.9674, 3.7504)
σ^2_{LPLS}	5.5790	(2.9693, 14.0854)	σ_{LPLS}	2.3620	(1.7232, 3.7530)
σ^2_L	5.3857	(2.8139, 14.1576)	σ_L	2.3207	(1.6775, 3.7627)
σ^2_{LS}	.1933	(.0997, .5234)	σ_{LS}	.4397	(.3157, .7234)
σ^2_W	1.0800	(.9213, 1.2839)	σ_W	1.0392	(.9598, 1.1331)

TABLE 7.155. ANALYSIS OF VARIANCE FOR LOG_e CADMIUM DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	269	1557.68	--	--
Leachate Samples	9	343.35	--	--
Laboratories	26	859.03	33.04	21.7*
Residual	234	355.29	1.52	--

* $P < .005$

TABLE 7.156. VARIANCE COMPONENT ESTIMATES FOR $\log_e$ CADMIUM DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	4.6720	(3.2813, 7.1865)	σ_R	2.1615	(1.8114, 2.6808)
σ^2_L	3.1520	(1.9150, 6.1360)	σ_L	1.7754	(1.3838, 2.4771)
σ^2*	1.5200	(1.2782, 1.8379)	σ**	1.2329	(1.1306, 1.3557)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Copper Data Base

Data were received from 29 of the 48 laboratories that agreed to perform the copper analysis. The analysis was performed in triplicate by 15 laboratories for all 10 leachate samples. A single value or an average value was reported by 11 laboratories. The remaining 3 laboratories reported an unequal number of replicates.

Sixty-six values ranging from .001 to .1 mg/ℓ were reported as detection limits (i.e., < value) by 9 laboratories. The difference in magnitude for these values is comparatively large. A complete listing of these values is given in Table A-13 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Forty-seven mg/ℓ concentration levels were reported for leachate samples A, B, C, D, E, F, G, H, I, and J with frequency 3, 4, 3, 3, 3, 3, 7, 7, 6, and 8, respectively. Four laboratories reported one or more zero concentration levels.

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.103. A regression equation was calculated to be $\sigma = .0903\ \mu + .00233$ with an R^2 value of 68%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .936 \log \mu - 1.02$ with an R^2 value of 82%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.58, 1.29), which suggests that a logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

A summary of the analytical results for the 10 leachate samples is given in Table 7.157 . The average copper concentration of the samples ranged from .0129 to .204 mg/ℓ, with the highest value generally 10 times larger than the lowest value for any particular leachate sample.

TABLE 7.157 SUMMARY OF ANALYTICAL RESULTS FOR COPPER DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	.145	0	.521	.13	.0259	.108
B	.115	0	.337	.0967	.0171	.0888
C	.113	0	.321	.119	.0109	.0629
D	.126	0	.301	.125	.02	.0632
E	.204	0	.389	.233	.0156	.0961
F	.199	0	.394	.214	.0171	.077
G	.0213	0	.0687	.02	.00117	.0169
H	.0184	0	.05	.016	.00386	.0139
I	.0129	0	.074	.02	.0047	.0166
J	.0205	0	.276	.01	.00304	.0507

*All entries in mg/ℓ.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.104. A regression equation was calculated to be $\sigma = .395\ \mu + .0204$ with an R^2 value of 72%. For the logarithms of these values, a regression equation was calculated to be $\log \sigma = .673 \log \mu - .533$ with an R^2 value of 77%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of $\log \mu$) is (.38, .97), which suggests that a square root or perhaps logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

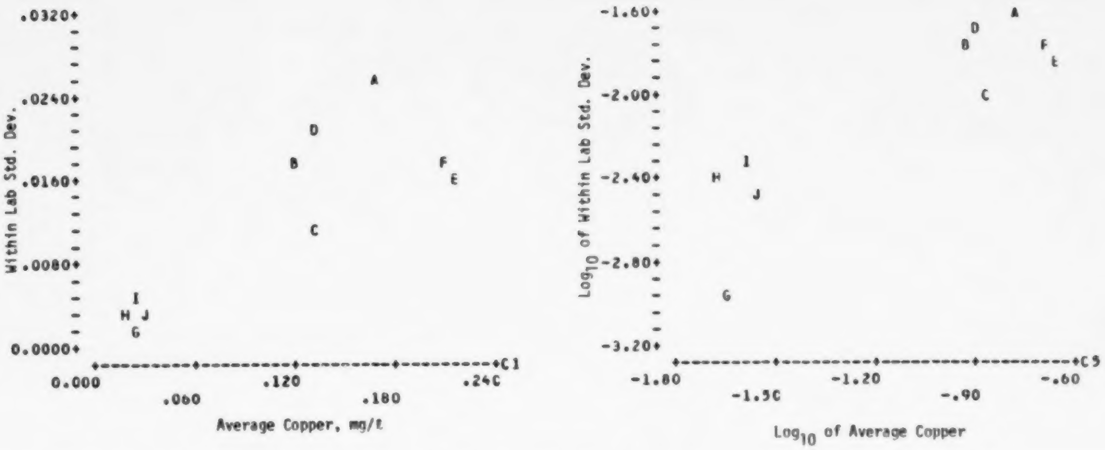

Figure 7.103. Relationship of the within laboratory standard deviation to the copper concentration level.

The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, .00025 was added to all zero values. These transformed data were used in the statistical analysis of this parameter.

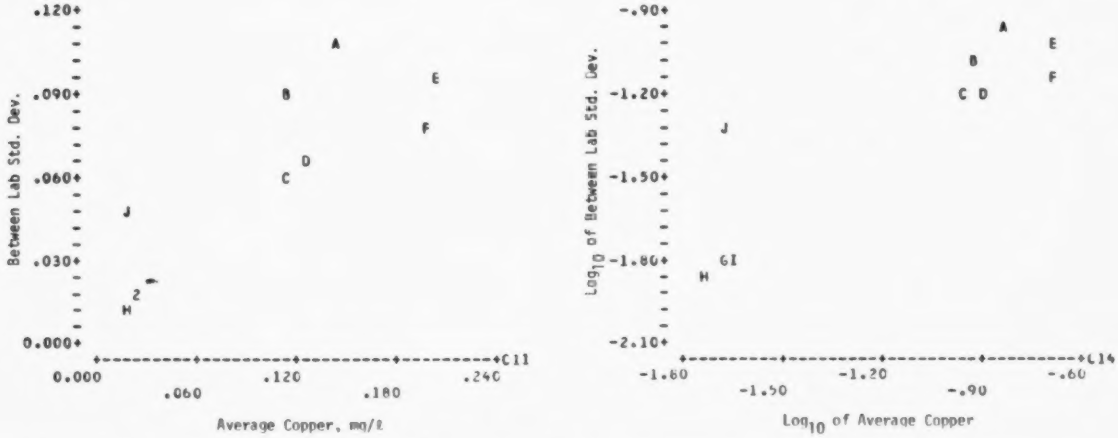

Figure 7.104. Relationship of the between laboratory standard deviation to the copper concentration level.

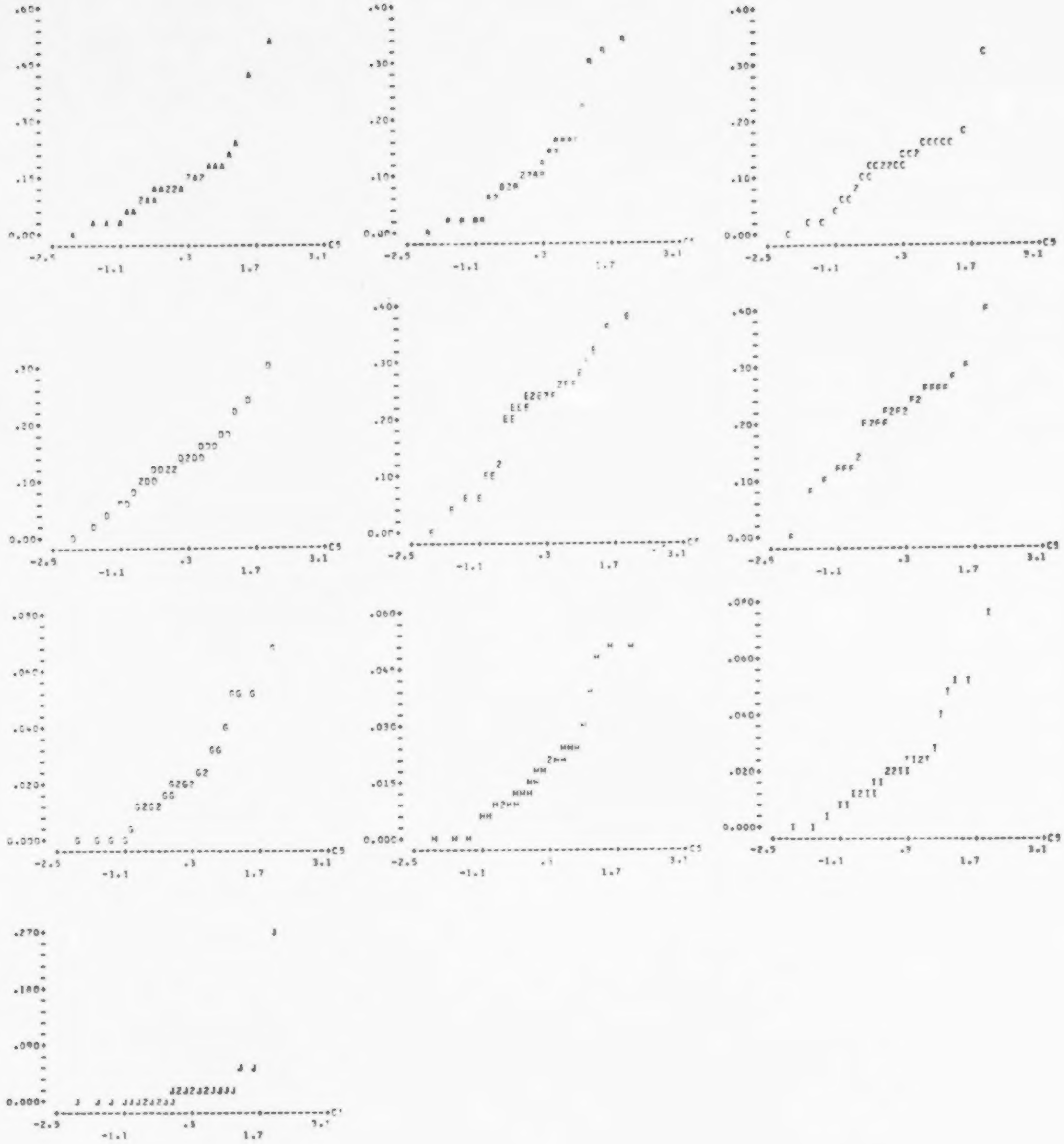

Figure 7.105. Ordered laboratory averages for copper data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

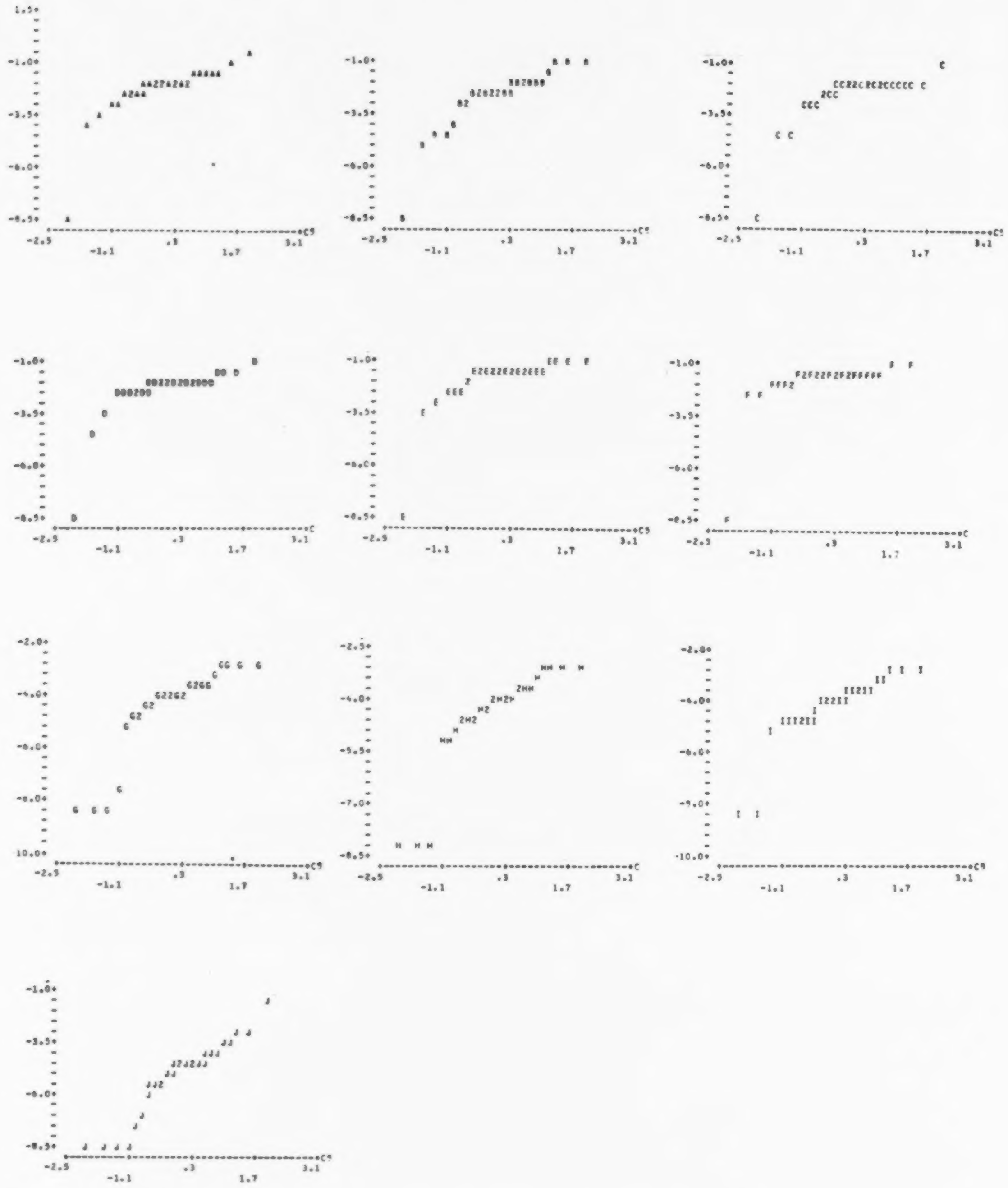

Figure 7.106. Ordered laboratory averages for $\log_e$ transformed copper data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J, respectively.

The ordered laboratory averages for the copper data plotted against the quantiles from a normal distribution are shown in Figure 7.105 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.106. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.158.

TABLE 7.158 R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average R^2	Std. dev. of R^2
	A	B	C	D	E	F	G	H	I	J		
Original	79	89	89	95	94	93	90	91	86	34	84	18
Transformed	62	75	59	54	51	39	75	74	73	92	65	15

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data (i.e., closer to a straight line). The lower R^2 values for 9 of the 10 leachate samples, and the lower average R^2 for the $\log_e$ transformed data than were obtained for the original data appears to be caused by the choice of the amount added to zero values before transforming. Several outlying averages are present in most of the leachate samples, however, which will affect the R^2 values for both the original and transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed copper data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 15 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.159. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.160.

TABLE 7.159. ANALYSIS OF VARIANCE FOR LOG_e COPPER DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	449	1926.9848	--	--
Leachate Samples	9	629.7902	--	--
Laboratories	14	1008.5252	72.0375	33.7*
Lab x Sample	126	269.7225	2.1407	33.9*
Residual	300	18.9469	.0632	--

* P < .005

TABLE 7.160. VARIANCE COMPONENT ESTIMATES FOR LOG_e COPPER DATA BASED ON LABORATORIES REPORTING 3 REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	3.0856	(1.8620, 6.0807)	σ_R	1.7566	(1.3645, 2.4659)
σ^2_{LPLS}	3.0224	(1.8074, 6.0574)	σ_{LPLS}	1.7385	(1.3444, 2.4612)
σ^2_L	2.3299	(1.2285, 6.0027)	σ_L	1.5264	(1.1084, 2.4500)
σ^2_{LS}	.6925	(.5452, .9090)	σ_{LS}	.8322	(.7384, .9534)
σ^2_W	.0632	(.0542, .0747)	σ_W	.2514	(.2328, .2733)

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.161. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.162.

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laobratories. The estimates obtained for this data set were: $\sigma_R = .60$, $\sigma_L = .31$, and $\sigma = .51$. These values are smaller than the corresponding estimates given in Table 7.162, which indicates that greater precision may be attainable.

TABLE 7.161 ANALYSIS OF VARIANCE FOR LOG_e COPPER DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	289	961.058	--	--
Leachate Samples	9	396.662	--	--
Laboratories	28	385.928	13.783	19.5*
Residual	252	178.467	.708	--

* $P < .005$

TABLE 7.162. VARIANCE COMPONENT ESTIMATES FOR LOG_e COPPER DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	2.0155	(1.4461, 3.0046)	σ_R	1.4197	(1.2025, 1.7334)
σ^2_L	1.3075	(.8052, 2.4855)	σ_L	1.1435	(.8973, 1.5765)
σ^2*	.7080	(.5990, .8499)	σ**	.8414	(.7739, .9219)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

Nickel Data Base

Data were received from 28 of the 48 laboratories that agreed to perform the nickel analysis. The analysis was performed in triplicate by 13 laboratories and in duplicate by 1 laboratory for all 10 leachate samples. A single value or an average value was reported by 11 laboratories. The remaining 3 laboratories reported an unequal number of replicates.

Thirty-two values ranging from .01 to .1 mg/ℓ were reported as detection limits (i.e., < value). The difference in magnitude for these values is comparatively large. A complete listing of these values is given in Table A-14 of Appendix A, along with their frequency of occurrence, the laboratories reporting these values, and the leachate samples in which these values occurred. Half the reported detection limit value was used in the data base for all statistical analyses. Thirty-six mg/ℓ concentration levels were reported for leachate samples B, D, E, F, G, H, I, and J, with frequency 3, 3, 3, 4, 3, 6, 3, and 11, respectively. Five laboratories reported one or more zero concentration levels.

A summary of the analytical results for the 10 leachate samples is given in Table 7.163. The average nickel concentration of the samples ranged from .0353 to 3.71 mg/ℓ, with the highest value generally 10 times larger than the lowest value for any particular leachate sample.

TABLE 7.163. SUMMARY OF ANALYTICAL RESULTS FOR NICKEL DATA*

Leachate sample	Grand sample average	Minimum lab average	Maximum lab average	Median of lab averages	Within lab std. dev.	Between lab std. dev.
A	3.71	1.57	26	2.72	.134	4.44
B	.172	0	.867	.147	.0121	.157
C	3.06	0.05	25.7	2.30	.0715	4.5
D	.367	0	1.1	.317	.0316	.232
E	.763	0	2.87	.705	.0309	.457
F	.144	0	.483	.123	.0174	.0935
G	.205	0	2.37	.1	1.0	.436
H	.0824	0	.7	.0409	.0133	.14
I	.149	0	.367	.123	.0117	.0829
J	.0353	0	.2	.0168	.00306	.0503

*All entries in mg/ℓ

Distribution of the Data

The pooled within laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.107 A regression equation was calculated to be $\sigma = -.0078\ \mu + .141$ with an R^2 value of 0%. For the logarithms of these values, a regression equation was calculated to be log σ = .627 log μ - 1.22 with an R^2 value of 34%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of log μ) is (-.09, 1.35), which suggests that a square root or perhaps logarithmic transformation of the data should make the within laboratory variances at different concentration levels approximately equal for the transformed data.

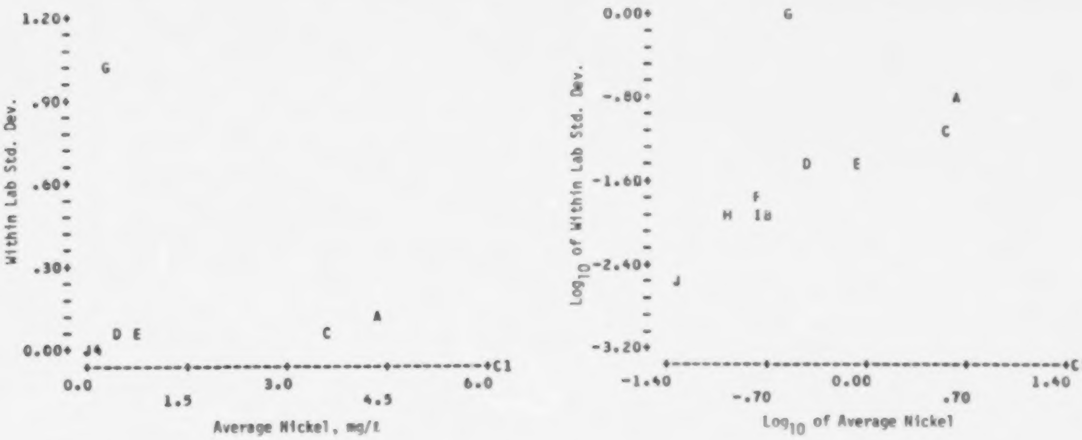

Figure 7.107 Relationship of the within laboratory standard deviation to the nickel concentration level.

The between laboratory standard deviation plotted against the average and the logarithms of these values are shown in Figure 7.108 A regression equation was calculated to be σ = 1.32 μ - .086 with an R^2 value of 97%. For the logarithms of these values, a regression equation was calculated to be log σ = .992 log μ + .0007 with an R^2 value of 90%. A 95% confidence interval for the estimated power to which μ is raised (i.e., the coefficient of log μ) is (.73, 1.26), which suggests that a logarithmic transformation of the data should make the between laboratory variances at different concentration levels approximately equal for the transformed data.

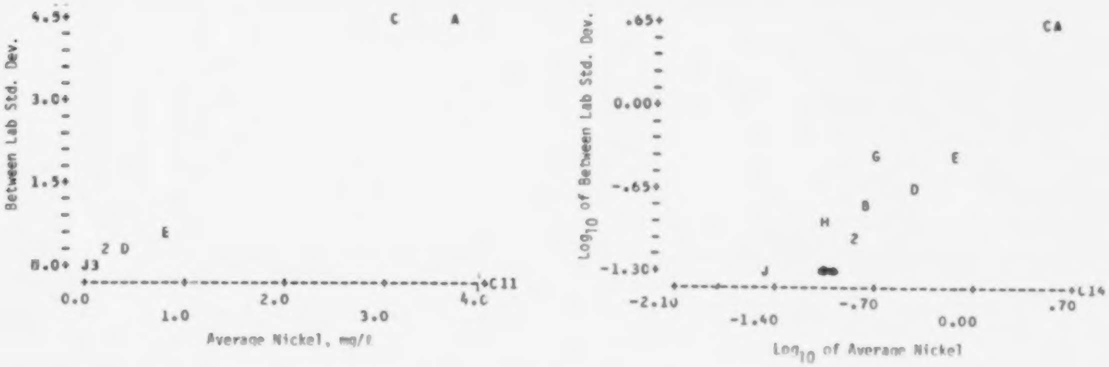

Figure 7.108 Relationship of the between laboratory standard deviation to the nickel concentration level.

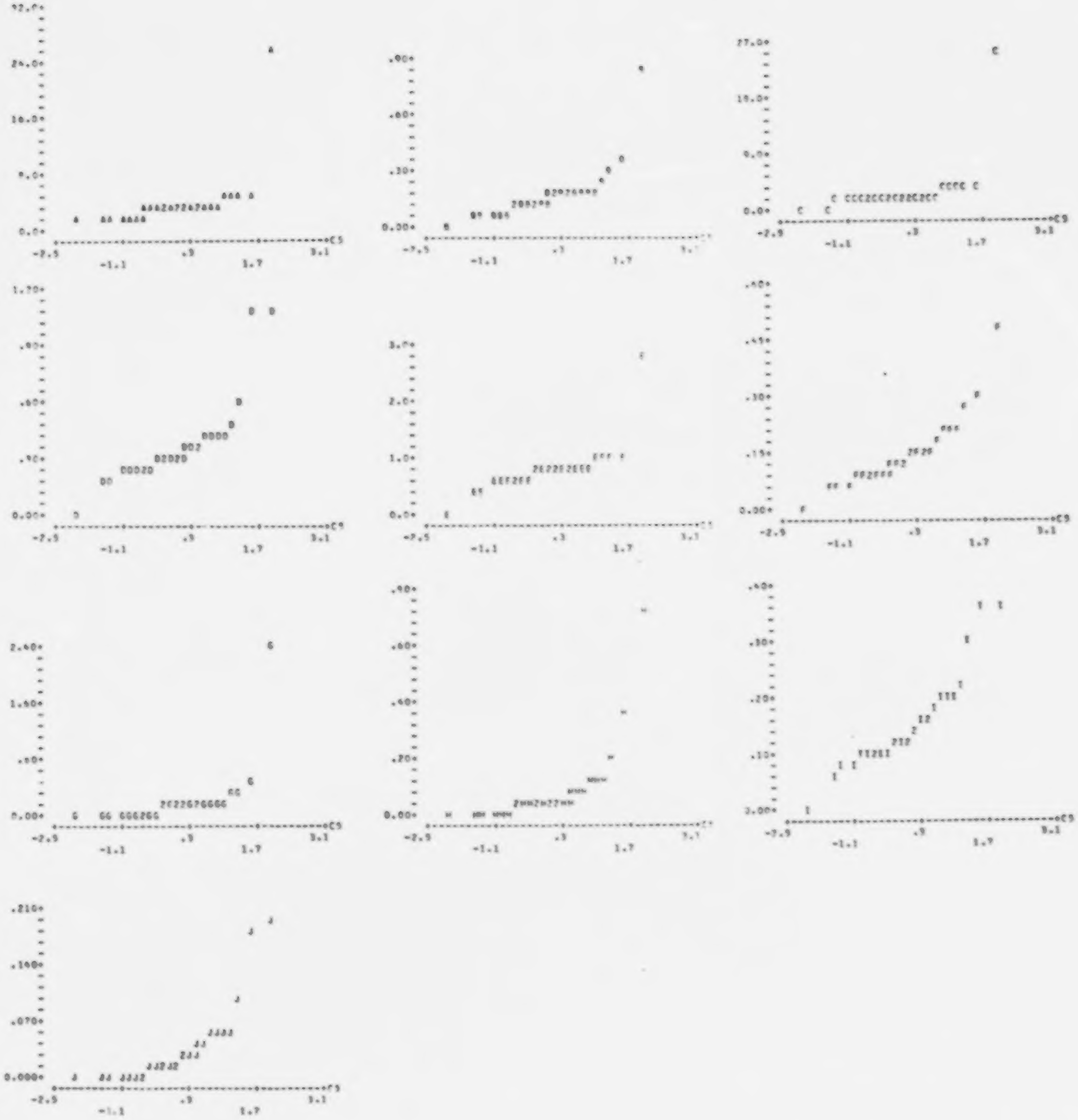

Figure 7.109. Ordered laboratory averages for nickel data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J respectively.

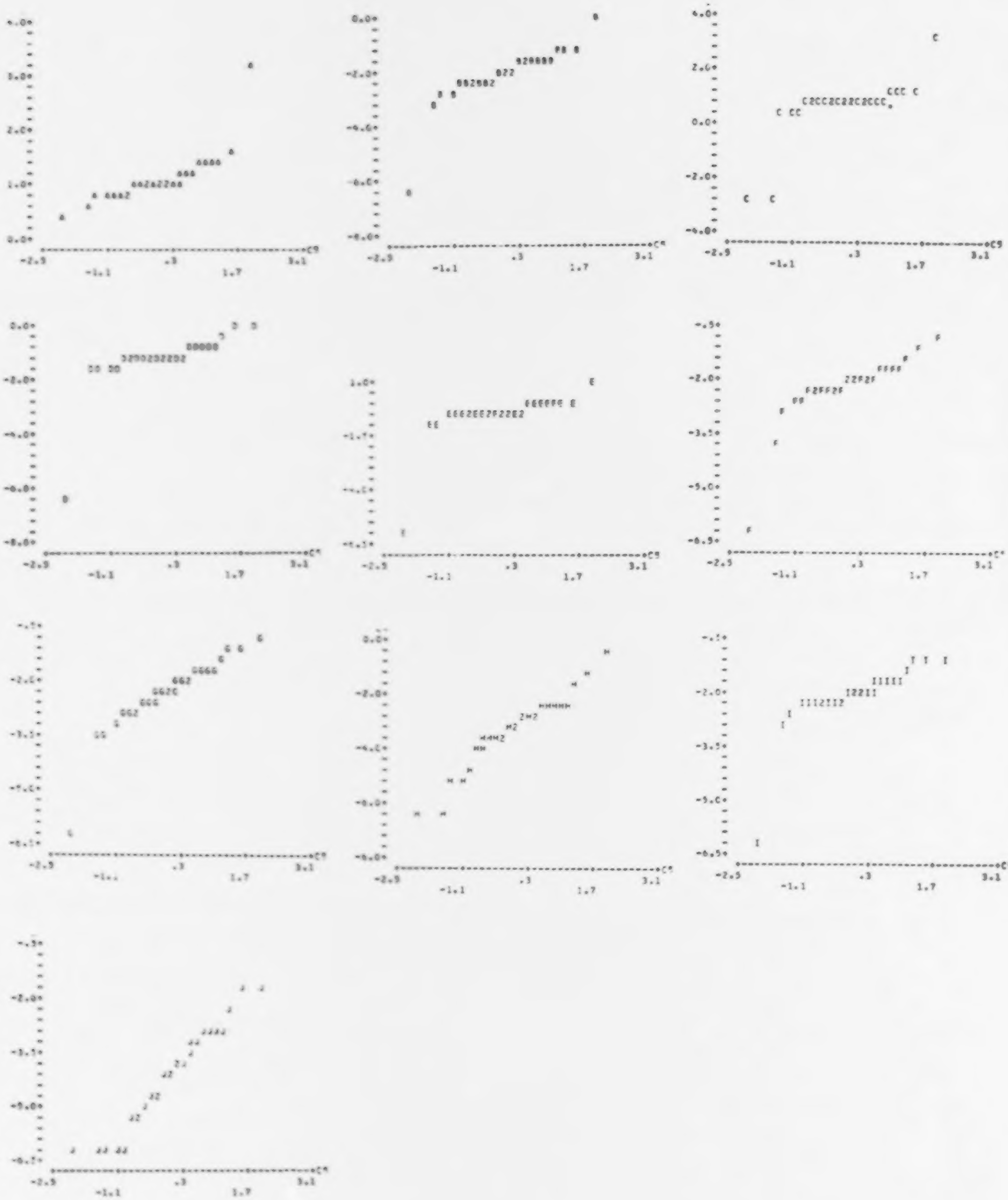

Figure 7.110. Ordered laboratory averages for $\log_e$ transformed nickel data (vertical axis) plotted against quantiles from a normal distribution (horizontal axis) for leachate samples A through J respectively.

Although the square root transformation was indicated to stabilize the within laboratory variance, the appearance of the graphs and low R^2 value makes the choice of a transformation uncertain. The natural logarithms of the reported concentration levels were taken to achieve homogeneity of the within and between laboratory variances. Before applying the transformation, .002 was added to all zero values. These transformed data were used in the statistical analysis of this parameter.

The ordered laboratory averages for the nickel data plotted against the quantiles from a normal distribution are shown in Figure 7.109 for the 10 leachate samples A through J. The corresponding plots for the $\log_e$ transformed data are shown in Figure 7.110. The R^2 values of a simple linear regression equation fitted to each sample for both the original and $\log_e$ transformed data are given in Table 7.164.

TABLE 7.164. R^2 VALUES OF REGRESSION FOR QUANTILE-QUANTILE PLOTS

Data	Leachate Sample										Average	Std. dev.
	A	B	C	D	E	F	G	H	I	J	R^2	of R^2
Original	31	63	29	70	54	81	34	50	87	66	57	21
Transformed	68	75	55	51	39	71	84	95	63	96	70	19

For the original data it appears that the distribution of the laboratory averages has a heavier upper tail than the upper tail of a normal distribution. The distribution of the $\log_e$ transformed data appears closer to that of a normal distribution than the distribution of the original data, (i.e. closer to a straight line). This observation is supported by the higher R^2 values for 6 of the ten leachate samples, the greater average R^2, and smaller standard deviation of the R^2 values for the $\log_e$ transformed data than were obtained for the original data. Outlying averages are present in most of the leachate samples however, which will affect the R^2 values for both the original and transformed data. Additionally, the choice of the amount added to zero values before transforming appears to have caused lower R^2 values for the $\log_e$ transformed data.

Variance Component Estimates

The variance component estimates that follow are for the $\log_e$ transformed nickel data, and thus the resulting standard deviations can be interpreted as estimates of coefficient of variations in the original scale of measurement.

The data from 13 laboratories were used to form a balanced data set having 3 replicates for all 10 leachate samples. The results of the analysis of variance performed on this data set are given in Table 7.165. The hypothesis that the between laboratory variance component is zero is strongly rejected. The hypothesis that the laboratory sample interaction variance component is zero is also strongly rejected. The variance component estimates obtained for this data set are given in Table 7.166.

TABLE 7.165. ANALYSIS OF VARIANCE FOR LOG_e NICKEL DATA BASED ON 3 REPLICATES

Source	d.f.	Sum of Squares	Mean Square	F
Total	389	1643.505	--	--
Leachate Samples	9	927.283	103.031	--
Laboratories	12	437.400	36.450	16.1*
Lab x Sample	108	244.131	2.260	17.0*
Residual	260	34.691	.133	--

* $P < .005$

The results of the analysis of variance performed on the averages from all reporting laboratories are given in Table 7.167. The hypothesis that the between laboratory variance component is zero is strongly rejected. The variance component estimates obtained for this data set are given in Table 7.168

The analysis of variance was performed on the laboratory averages after omitting the data from visually outlying laboratories. The estimates obtained for this data set were: $\sigma_R = .57$, $\sigma_L = .30$, and $\sigma = .48$. These values are smaller than the corresponding estimates given in Table 7.168, which indicates that greater precision may be attainable.

TABLE 7.166. VARIANCE COMPONENT ESTIMATES FOR LOG_e NICKEL DATA BASED ON LABORATORIES REPORTING THREE REPLICATES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.9817	(1.2717, 3.5116)	σ_R	1.4077	(1.1277, 1.8739)
σ^2_{LPLS}	1.8487	(1.1538, 3.4336)	σ_{LPLS}	1.3597	(1.0741, 1.8530)
σ^2_L	1.1397	(.5650, 3.3801)	σ_L	1.0676	(.7516, 1.8385)
σ^2_{LS}	.7090	(.5442, .9625)	σ_{LS}	.8420	(.7377, .9810)
σ^2_W	.1330	(.1128, .1592)	σ_W	.3647	(.3359, .3990)

TABLE 7.167 ANALYSIS OF VARIANCE FOR LOG_e NICKEL DATA BASED ON LABORATORY AVERAGES

Source	d.f.	Sum of Squares	Mean Square	F
Total	279	1005.582	--	--
Leachate Samples	9	692.632	--	--
Laboratories	27	161.382	5.977	9.58*
Residual	243	151.569	.624	--

* $P < .005$

TABLE 7.168. VARIANCE COMPONENT ESTIMATES FOR LOG_e NICKEL DATA BASED ON LABORATORY AVERAGES

	Estimate	95% Conf. Int.		Estimate	95% Conf. Int.
σ^2_R	1.1593	(.8862, 1.5822)	σ_R	1.0767	(.9414, 1.2578)
σ^2_L	.5353	(.3189, 1.0804)	σ_L	.7316	(.5647, 1.0394)
σ^2*	.6240	(.5264, .7517)	σ**	.7899	(.7255, .8670)

* $\sigma^2 = \sigma^2_{LS} + \sigma^2_W$

** $\sigma = \sqrt{\sigma^2_{LS} + \sigma^2_W}$

SECTION 8

LEACHATE RECOVERY STUDIES

Recovery studies were conducted by spiking sample F (then designated sample E) with selected chemicals to concentration increases of approximately 50%. The results in Table 8.1 show that the average analytical recovery for 24 parameters is 81% of the calculated added amounts. The range of recoveries is very large, from -138% to 314%.

The recovery of the organic parameters varied from 33% to 137%. The free volatile fatty acids, spiked as acetic and butyric acid, gave a recovery closest to 100%. The COD, however, had a low recovery of 33%, possibly indicating that the spiked acetic acid (886mg/ℓ), butyric acid (925mg/ℓ), glucose (1959 mg/ℓ), and glutamic acid (367 mg/ℓ) are incompletely oxidized during the test. Although theCOD/TOC was predicted to increase from 3.1 to 3.4 as a result of the spiking, it actually decreased to 1.54. The larger than 100% recovery for the TOC may have been due to the increase of the inorganic carbon added through Na_2CO_3 and $BaCO_3$. The low recovery for the volatile residue may indicate that substantial amounts of fatty acids already volatize below 105°C and are thus not counted in the residue determination. The larger than 100% recovery for the organic nitrogen was not noted before (Chian and DeWalle, 1975) but may be due to the distillation of substances, such as carbonates, that may interfere with the titration step.

The recovery of the anions varied from -32% to 245%. The high recovery of the ammonia nitrogen parallels that of the organic nitrogen and was not noted in earlier studies. It may also be due to organic'or inorganic substances that interfere with the titration step. The low recovery of the sulfate method may be due to the incomplete formation of the barium sulfate precipitate. In earlier studies (Chian and DeWalle, 1975), a larger than 100% sulfate recovery due to the inclusion of other precipitates was generally noted. The negative recovery of the phosphorus parallels that of the iron and may be due to the formation of an iron hydroxide precipitate causing absorption of the phosphates. The presence of such a precipitate in sample E was visually observed. Low phosphorus values may result from either incomplete resuspension before taking an aliquot or incomplete digestion of the precipitate. The larger than 100% recovery of the chloride may reflect the iron interference in the argentometric method. The potentiometric determination, on the other hand, gave close to 100% recovery. The high recovery in the alkalinity determination is likely due to the presence of free volatile fatty acids. Although the added carbonates increase the alkalinity by 146 mg/ℓ, partial titration of only 16% of the butric and acetic acid will increase the alkalinity by 262 mg/ℓ. The low recovery of the spiked nitrate is consistent with previous studies (Chian and DeWalle, 1975), as the substances in the leachate greatly interfere with the nitrate reduction step due to fouling of the column. The single high reading obtained with the specific ion electrode and the three high values with the brucine method indicate that these methods give higher recoveries than does the cadmium reduction method.

The recovery of the cations varies from -138% to 328%. The larger than 100% recovery of both sodium and potassium is likely due to the omission of cesium nitrate ($CsNO_3$) which suppresses the ionization of the analyte ion, especially when using an air-acetylene flame. The recovery of magnesium is close to 100%; the recovery of calcium barium and iron, however is less than 10% which may well be due to the formation of a precipitate likely consisting of $Fe(OH)_3$, $Ca(OH)_2$, $Ba(OH)$, $CaCO_3$, $CaSO_4$ and $BaSO_4$. Low analytical values may result from either incomplete resuspension before taking an aliquot or incomplete digestion of the precipitate. All of the heavy metals, with the exception of cadmium and nickel, experienced a recovery of less than 25%. The negative recovery of lead may indicate a high affinity to the formed precipitate and its incomplete release during the acid digestion. The larger than 100% recovery for cadmium may be due to its low concentration and the large standard deviation of the method.

	Parameter	Spiked Sample E	Unspiked Sample F	Measured Increase of Spiked Parameters	Calculated Increase of Spiked Parameters	Percentage Recovery
1	pH	6.49	6.82	-0.33	-	-
2	ORP	-138	-196	-58	-	-
3	Turbidity	349	560	-211	-	-
4	Conductivity	5003	3195	1818	-	-
5	Fatty Acids	1514	497	1017	1062	957
6	COD	3408	2047	1361	4136	32.9
7	TOC	2220	660	1560	1141	137
8	Total Residue	4155	2944	1211	4345	27.9
9	Volatile Residue	2168	1425	743	2660	27.9
10	Organic Nitrogen	168	107	61	35.5	172
11	Ammonia Nitrogen	103	38.2	64.8	26.4	245
12	Sulfate	112	29.5	82.5	156.5	52.7
13	Total Phosphorus	6.42	6.83	-0.41	1.3	-31.5
14	Chloride	275	107	168	97.7	172
15	Alkalinity	1963	1701	262	145.5	180
16	Nitrate Nitrogen	0.526	0.608	-0.82	0.65	-126
17	Sodium	229	103	126	66	191
18	Potassium	161	83	78	23.8	328
19	Calcium	698	675	23	263.3	8.7
20	Magnesium	99.6	60.7	38.9	35.5	109
21	Barium	2.05	1.87	0.18	2.7	6.7
22	Iron	161	172	-11	131.3	-84
23	Zinc	5.41	4.67	0.74	6.3	11.7
24	Lead	0.308	0.317	-0.09	0.065	-138
25	Chromium	0.228	0.080	0.148	0.580	25.5
26	Cadmium	0.033	0.010	0.022	0.007	314
27	Copper	0.204	0.199	0.005	0.035	14.3
28	Nickel	0.763	0.144	0.619	0.640	96.7
29	Average					81.0%

TABLE 8.1 RESULTS OF RECOVERY STUDIES USING A SPIKED AND UNSPIKED LEACHATE SAMPLE

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APPENDIX A: DETECTION LIMITS OF ANALYTICAL METHODS

TABLE A-1 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE FREE VOLATILE FATTY ACID DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
50	1	43	J
80	3	2	J
100	3	2	I

*Value reported in the form < "value".

TABLE A-2 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE AMMONIA NITROGEN DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
3	3	42	J

*Value reported in the form < "value".

TABLE A-3 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE SULFATE DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.5	2	50	H
4	15	2	B, D, G, H, J
5	24	12, 18, 19, 20	B, E, F, G, H, I, J

*Value reported in the form < "value".

TABLE A-4 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE TOTAL PHOSPHORUS DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.03	3	21	J
1	2	25	D, J

*Value reported in the form < "value".

TABLE A-5 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE CHLORIDE DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
1	1	43	H
6	3	20	I
30	9	9	A, B, C

*Value reported in the form < "value".

TABLE A-6 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE NITRATE DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.01	3	50	H
.02	28	23, 25	A, B, C, D, E, F, G, H, I, J
.05	4	12, 18	I
.1	76	2, 9, 21, 29, 34, 43, 46	A, B, C, D, E, F, G, H, I, J

*Value reported in the form < "value".

TABLE A-7 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE MAGNESIUM DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
2	1	21	J

*Value reported in the form < "value".

TABLE A-8 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE BARIUM DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.1	6	30	F, G
.2	5	37	A, F, G, H, I
.5	9	23, 29	F, G, J
1	1	34	A

*Value reported in the form < "value".

TABLE A-9 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE ZINC DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.01	1	19	I
.02	1	10	I

*Value reported in the form < "value".

TABLE A-10 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE LEAD DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.02	15	50	B, G, H, I, J
.025	4	46	H, J
.03	3	19	H, I, J
.05	6	25	C, F, G, H, I, J
.1	5	23, 29	G, H, I
.2	24	12	B, D, E, F, G, H, I, J
.5	24	15	B, D, E, F, G, H, I, J

* Value reported in the form < "value".

TABLE A-11 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE CHROMIUM DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.005	3	28	J
.01	4	2	H, J
.02	21	25, 50	B, C, D, F, G, H, I, J
.04	9	30	H, I, J
.1	47	12, 15, 29	B, D, E, F, G, H, I, J

* Value reported in the form < "value".

TABLE A-12 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE CADMIUM DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.0005	1	23	J
.001	1	34	J
.002	22	13, 30	B, F, G, H, I, J
.003	1	34	F
.004	18	2	B, F, G, H, I, J
.005	9	28, 46	H, I, J
.01	68	12, 19, 21, 23, 25, 50	B, C, D, E, F, G, H, I, J
.02	3	29	H, I, J

*Value reported in the form < "value".

TABLE A-13 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE COPPER DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.001	6	1	G, J
.005	3	46	J
.01	7	19, 50	G, H, I, J
.02	16	21, 25	B, C, D, G, H, I, J
.05	16	12, 29	G, H, I, J
.1	18	15	B, E, G, H, I, J

*Value reported in the form < "value".

TABLE A-14 VALUES REPORTED IN THE FORM OF A DETECTION LIMIT FOR THE NICKEL DATA*

Reported Value	Frequency	Laboratory Numbers	Leachate Samples
.01	3	10, 23	H, J
.02	9	21, 30	H, J
.03	1	19	J
.05	14	12, 29, 50	B, G, H, J
.06	1	18	J
.1	4	25	C, F, G, H

*Value reported in the form < "value".

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APPENDIX C. METHODS, RANK SUMS, AND LABORATORY AVERAGES

TABLE C-1-1 METHOD USED IN THE DETERMINATION OF pH

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Electrometric Determination	29	35.5 to 253.5

TABLE C-1-3 . LABORATORY RANK SUMS FOR pH DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	126.5	15	66	37	104.5
2	116.5	18	235.5	40	253.5
4	39.5	19	90.5	42	59
7	250.5	20	193	43	149.5
8	209	21	35.5	46	152.5
9	199	23	228.5	48	207
10	191	25	112	49	179.5
12	115.5	28	180	50	164.5
13	168	29	139	51	54.5
14	95	34	235		

TABLE C-2-1 METHODS USED IN THE DETERMINATION OF ORP

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Platinum Electrode with Calomel Reference Electrode	9	13 to 96.5
-1	Not Specified	2	70 to 72

TABLE C-1-2 ORDERED LABORATORY RANK SUMS FOR pH DATA

Ordered Rank Sums	Method Code Number 1
35.5	21
39.5	4
54.5	51
59	42
66	15
---------*	
90.5	19
95	14
104.5	37
112	25
115.5	12
116.5	2
126.5	1
139	29
149.5	43
152.5	46
164.5	50
168	13
179.5	49
180	28
191	10
193	20
199	9
207	48
209	8
---------*	
228.5	23
235	34
235.5	18
250.5	7
253.5	40

*Rank sums below 73 or above 227 are extreme scores.

TABLE C-2-2 ORDERED LABORATORY RANK SUMS FOR ORP DATA

Ordered Rank Sums	Method Code Number -1	Method Code Number 1
13		15
--------*		
40		46
42		2
42		28
45		10
55		1
70	4	
72	9	
--------*		
90		14
94.5		50
96.5		51

*Rank sums below 33 or above 87 are extreme scores.

There does not appear to be any systematic difference between the Platinum Electrode method and the "unspecified" method. This conclusion is tenuous however as only two laboratories used the "unspecified" method.

TABLE C-2-3. LABORATORY RANK SUMS FOR ORP DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	55	10	45	46	40
2	42	14	90	50	94.5
4	70	15	13	51	96.5
9	72	28	42		

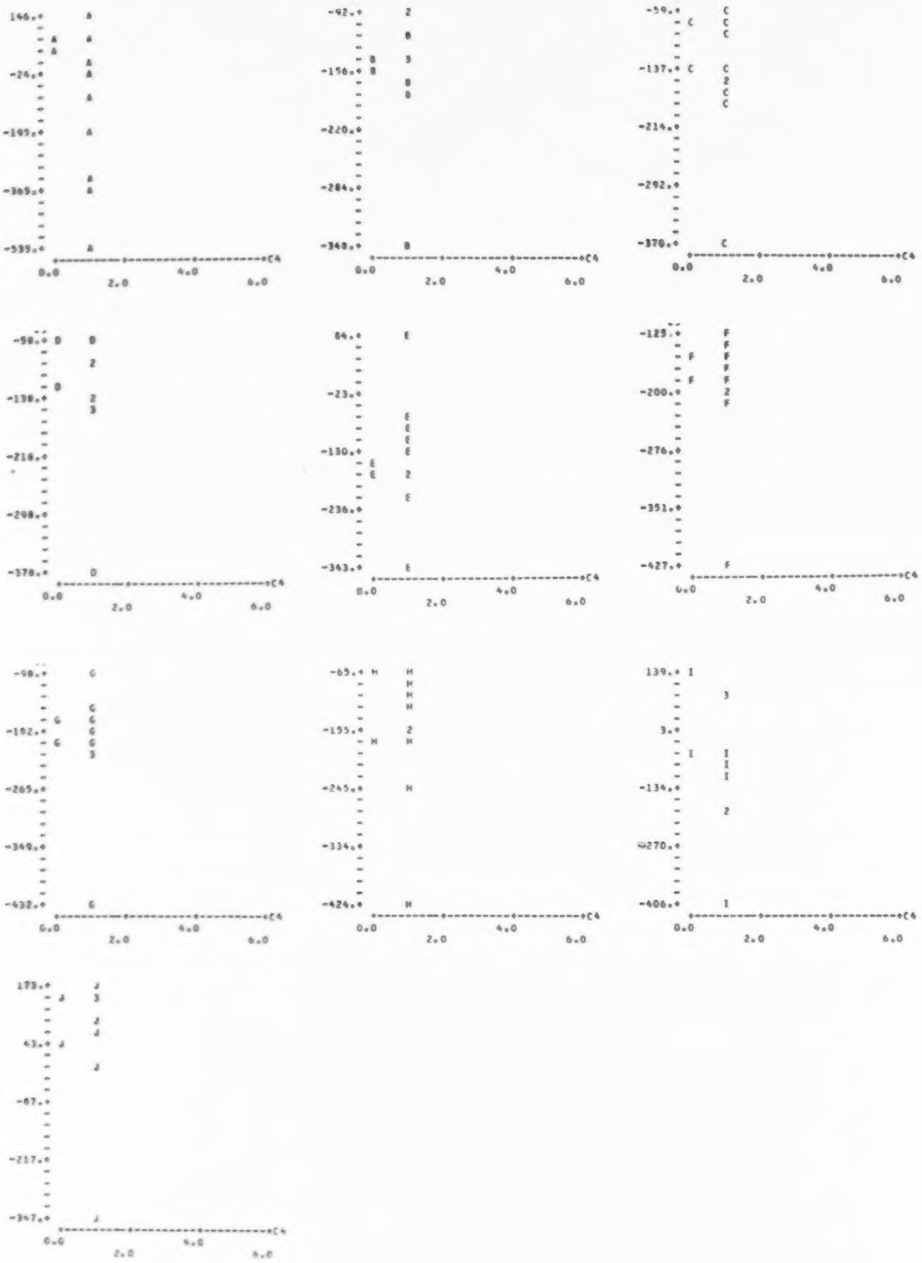

Figure C-1 Laboratory averages for ORP data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively. Method code number (-1) is plotted as a zero (0) in this figure.

TABLE C-3-1 METHODS USED IN THE DETERMINATION OF TURBIDITY

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Nephelometric (NTU's)	19	20.5 to 190
2	Visual-Jackson Turbidity Units (JTU's)	3	74.5 to 196

TABLE C-3-2 ORDERED LABORATORY RANK SUMS FOR LOG_e TURBIDITY DATA

Ordered Rank Sums	Method Code Number 1	2
20.5	4	
38.5	43	
52	1	
--------*		
61.5	28	
74.5		48
76.5	7	
77	25	
80.5	40	
83.5	34	
103.5	50	
111	29	
115.5	37	
134	49	
138	33	
143.5	10	
144.5	9	
166.5	2	
168	46	
--------*		
173	14	
182		8
190	23	
196		20

*Rank sums below 58 or above 172 are extreme scores.

The high rank sums scored by 2 of the 3 laboratories using the Visual-Jackson Turbidity Unit method gives some indication that this method yields higher turbidity readings than the Nephelometric method. The other laboratory using the Visual method scored a much lower rank sum which makes this conclusion rather tenuous however.

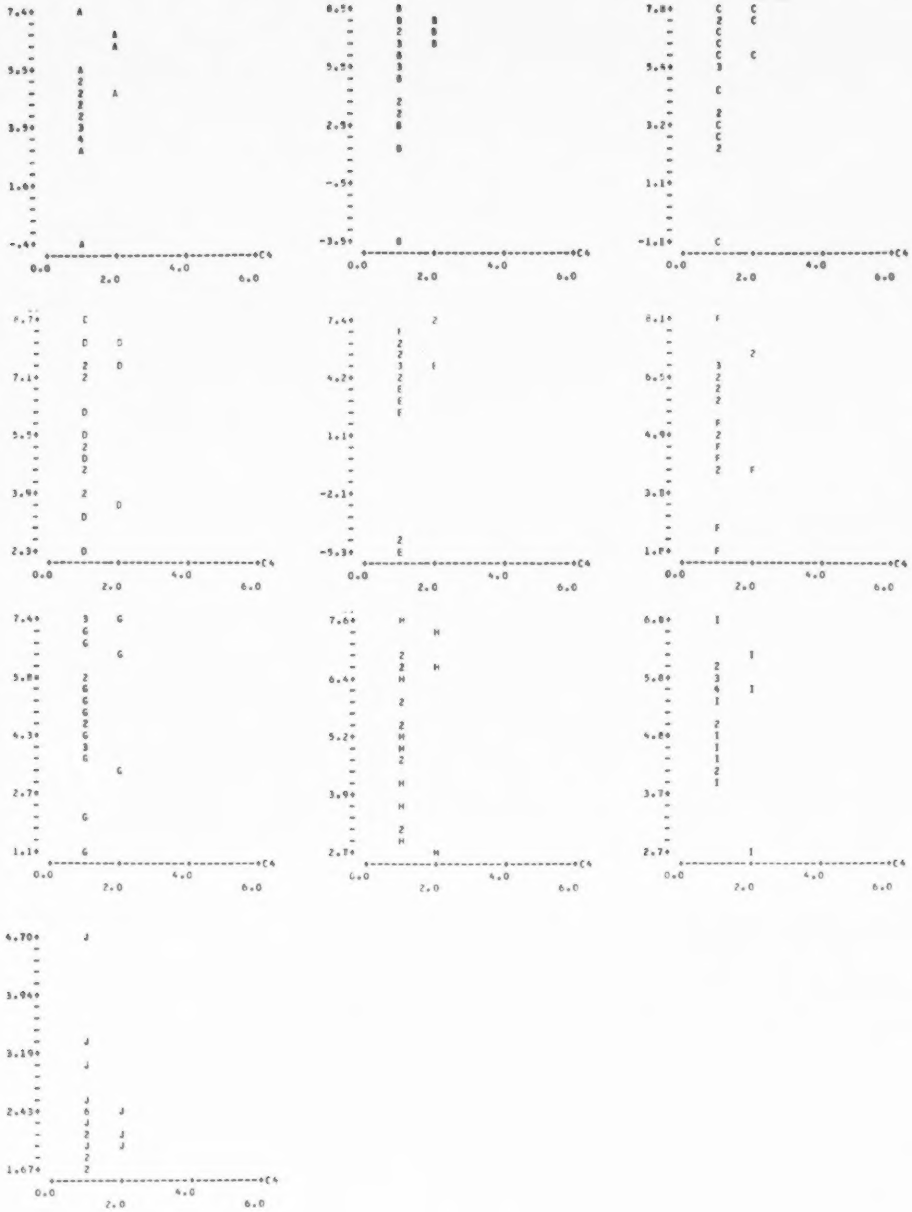

Figure C-2 Laboratory averages for $\log_e$ transformed turbidity data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-3-3. LABORATORY RANK SUMS FOR LOG_e TURBIDITY DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	52	20	196	37	115.5
2	166.5	23	190	40	80.5
4	20.5	25	77	43	38.5
7	76.5	28	61.5	46	168
8	182	29	111	48	74.5
9	144.5	33	138	49	134
10	143.5	34	83.5	50	103.5
14	173				

TABLE C-4-1. METHODS USED IN THE DETERMINATION OF CONDUCTIVITY

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Conductivity Bridge (Wheatstone Bridge)	20	36.5 to 235
2	Conductivity Cell (Platinum Electrode)	5	93.5 to 238
3	Not Specified	4	84 to 240

TABLE C-4-2 ORDERED LABORATORY RANK SUMS FOR LOG_e CONDUCTIVITY DATA

Ordered Rank Sums	Method Code Number 1	2	3
36.5	4		
40	42		
52	9		
60	12		
--------*			
73	51		
79.5	33		
84			29
93.5		48	
107	48		
109	14		
122.5	25		
132	8		
134.5	1		
166		20	
167	15		
172	18		
181.5	7		
183		43	
188	34		
191	37		
194	21		
197.5	19		
207.5			40
209			23
--------*			
228	49		
229		2	
235	10		
238		50	
240			28

* Rank sums below 73 or above 227 are extreme scores.

The Conductivity Bridge method and the Conductivity Cell method appear to give similar results. The "unspecified" method appears to yield slightly higher results than the other methods.

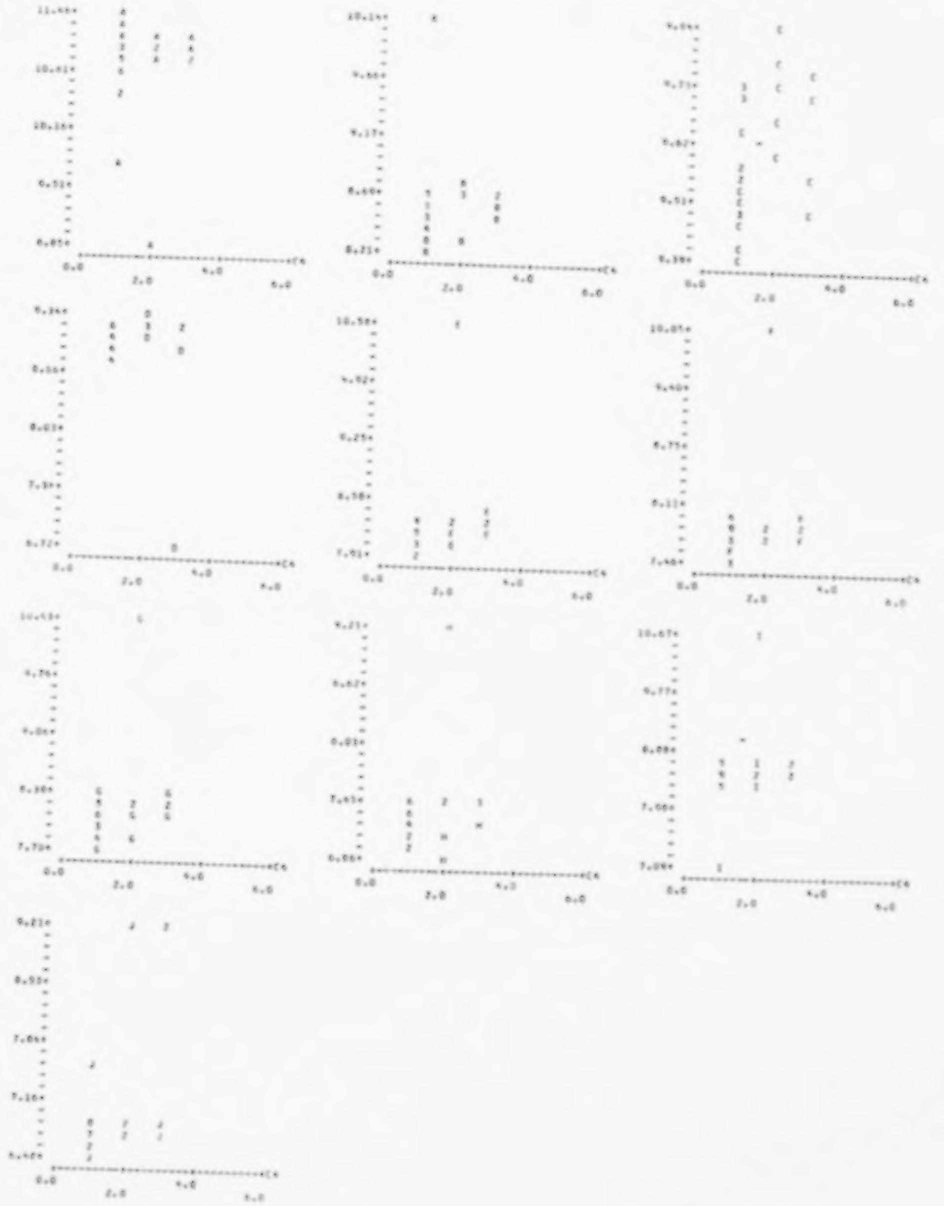

Figure C-3. Laboratory averages for $\log_e$ transformed conductivity data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-4-3. LABORATORY RANK SUMS FOR $\log_e$ CONDUCTIVITY DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	134.5	18	172	37	191
2	229	19	197.5	40	207.5
4	36.5	20	166	42	40
7	181.5	21	194	43	183
8	132	23	209	46	107
9	52	25	122.5	48	93.5
10	235	28	240	49	228
12	60	29	84	50	238
14	109	33	79.5	51	73
15	167	34	188		

TABLE C-5-1. METHODS USED IN THE DETERMINATION OF FREE VOLATILE FATTY ACIDS

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Chromatographic Separation	9	37 to 106
3	Steam Distillation	1	53
4	Gas Chromatography	1	81
-1	Not Specified	1	18

The Chromatographic Separation, Steam Distillation, and Gas Chromatography methods appear to give similar results. The "unspecified" method appears to yield lower results than the other methods. These conclusions are quite tenuous however as only the Chromatographic Separation method was performed by more than one laboratory.

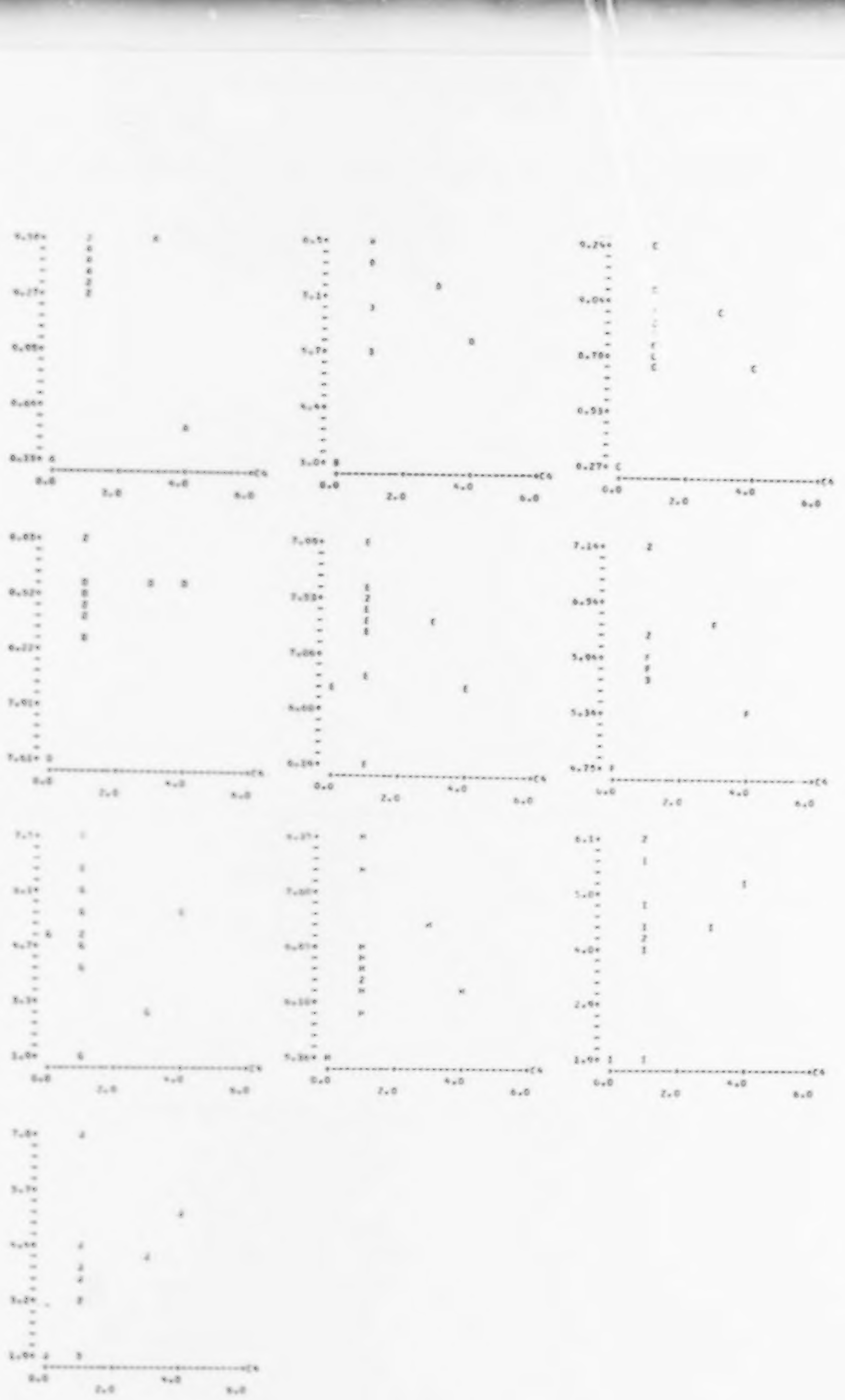

Figure C-4 Laboratory averages for $\log_e$ transformed free volatile fatty acids data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J, respectively. Method code number (-1) is plotted as a zero (0) in this figure.

TABLE C-5-2 ORDERED LABORATORY RANK SUMS FOR LOG_e FREE VOLATILE FATTY ACIDS DATA

Ordered Rank Sums	Method Code Number -1	1	3	4
18	42			
--------*				
37		51		
38.5		4		
49.5		1		
50		2		
53			9	
73		43		
77		46		
81				10
92		28		
--------*				
105		15		
106		14		

* Rank sums below 35 or above 95 are extreme scores.

TABLE C-5-3 LABORATORY RANK SUMS FOR LOG_e FREE VOLATILE FATTY ACIDS DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	49.5	10	81	42	18
2	50	14	106	43	73
4	38.5	15	105	46	77
9	53	28	92	51	37

TABLE C-6-1 METHODS USED IN THE DETERMINATION OF COD

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Manual Dichromate Reflux	23	43 to 245
2	Automated Dichromate Reflux	1	44.5
-1	Not Specified	1	178

TABLE C-6-2 ORDERED LABORATORY RANK SUMS FOR LOG_e COD DATA

Ordered Rank Sums	Method Code Number		
	-1	1	2
43		34	
44.5			49
50		9	
57.5		29	

98		15	
99		37	
102		4	
103		7	
105		48	
107		14	
110		46	
110		8	
125.5		12	
134		23	
137.5		1	
141		1	
155		51	
156		40	
174.5		21	
178	19		
185.5		50	
189		42	
191		10	
-------*			
209		25	
245		20	

* Rank sums below 64 or above 196 are extreme scores.

The low rank sum scored by the laboratory using the Automated Dichromate Reflux method. This conclusion is very tenuous however as only one laboratory used the Automated method. The "unspecified" method and Manual Dichromate Reflux method appear to give similar results.

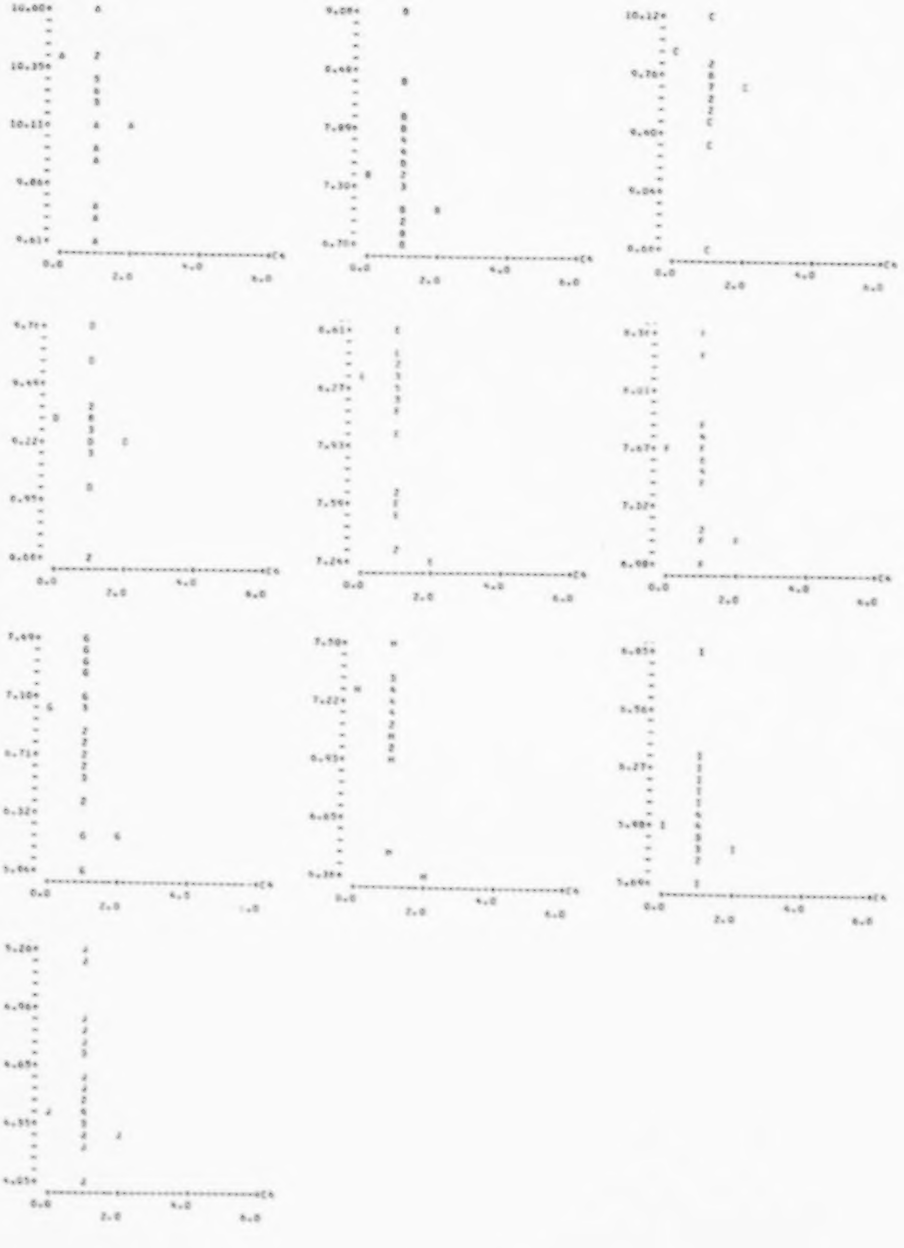

Figure C-5. Laboratory averages for $\log_e$ transformed COD data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J, respectively. Method code number (-1) is plotted as a zero (0) in this figure.

TABLE C-6-3. LABORATORY RANK SUMS FOR LOG_e COD DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	137.5	15	98	37	99
2	141	19	178	40	156
4	102	20	245	42	189
7	103	21	174.5	46	110
8	110	23	134	48	105
9	50	25	209	49	44.5
10	191	29	57.5	50	185.5
12	125.5	34	43	51	155
14	107				

TABLE C-7-1 METHODS USED IN THE DETERMINATION OF TOC

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Combustion - Infrared	21	55 to 203
2	Flame Ionization	1	114

TABLE C-7-3. LABORATORY RANK SUMS FOR LOG_e TOC DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	186	18	143	37	203
2	144	19	69	43	130.5
3	114	21	95	48	9
4	75	23	163.5	48	88.5
9	63	28	55	49	55
10	107	29	137	50	107
12	161	34	120	51	114.5
14	94				

TABLE C-7-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ TOC DATA

Ordered Rank Sums	Method Code Number 1	2
55	28	
55	49	
--------*		
63	9	
69	19	
75	4	
88.5	48	
94	14	
95	21	
105	46	
107	10	
107	50	
114		3
114.5	51	
120	34	
130.5	43	
137	29	
143	18	
144	2	
161	12	
163.5	23	
--------*		
186	1	
203	37	

* Rank sums below 58 or above 172 are extreme scores.

The Combustion-Infrared and Flame Ionization methods appear to give similar results. This conclusion is very tenuous however as the Flame Ionization method was performed by only one laboratory.

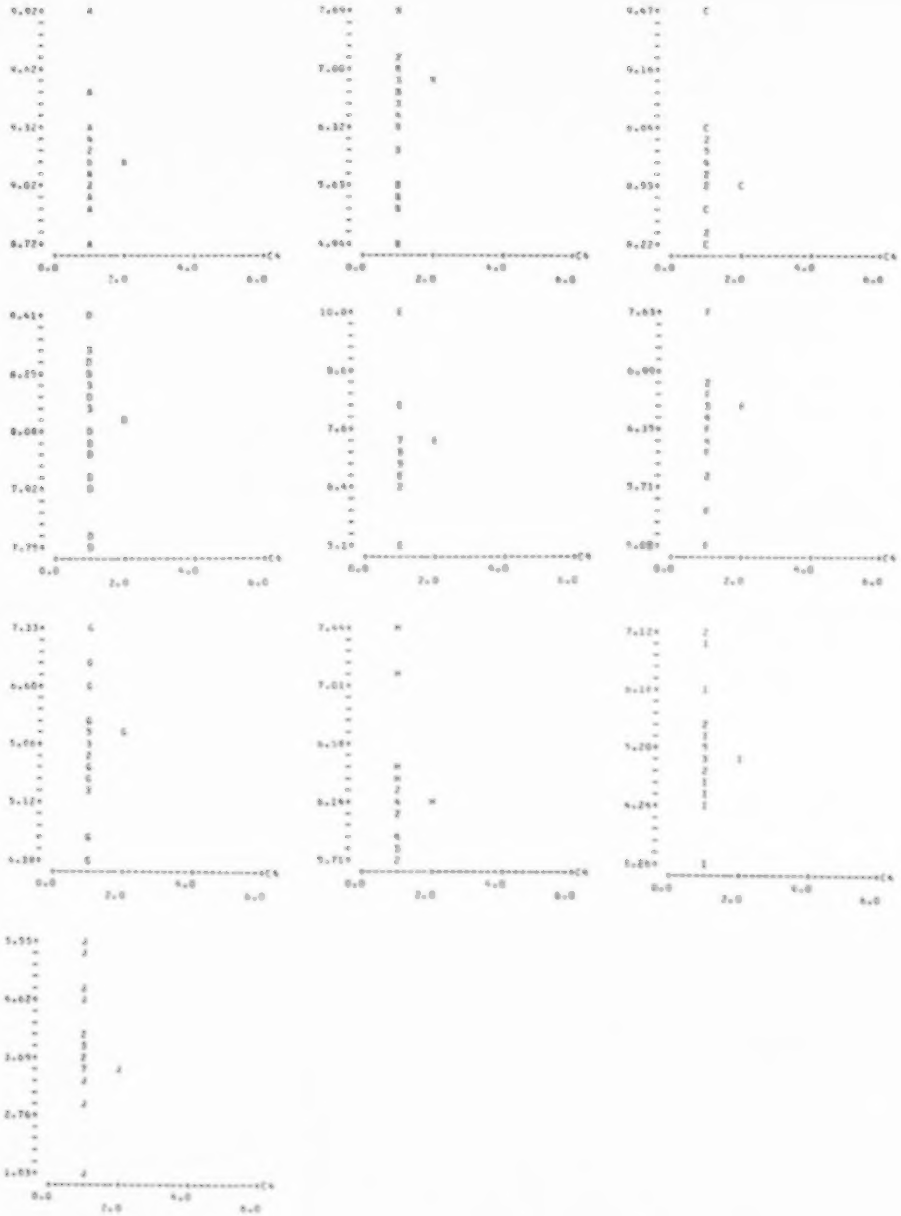

Figure C-6. Laboratory averages for $\log_e$ transformed TOC data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J, respectively.

TABLE C-8-1 METHODS USED IN THE DETERMINATION OF TOTAL RESIDUE

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Total Residue Dried at 103-105°C	26	10 to 244
2	Total Residue Dried at 180°C	2	25 and 38

TABLE C-8-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ TOTAL RESIDUE DATA

Ordered Rank Sums	Method Code Number 1	2
10	4	
25		48
38		49
-------*		
79	33	
88	18	
97	15	
101	37	
103	34	
109.5	10	
114	7	
134	8	
144	23	
149	29	
150	25	
151	46	
165	20	
167	43	
175	13	
179	12	
185	40	
187.5	21	
191	42	
195	19	
200	1	
216	2	
-------*		
231	14	
232	28	
244	9	

* Rank sums below 71 or above 219 are extreme scores.

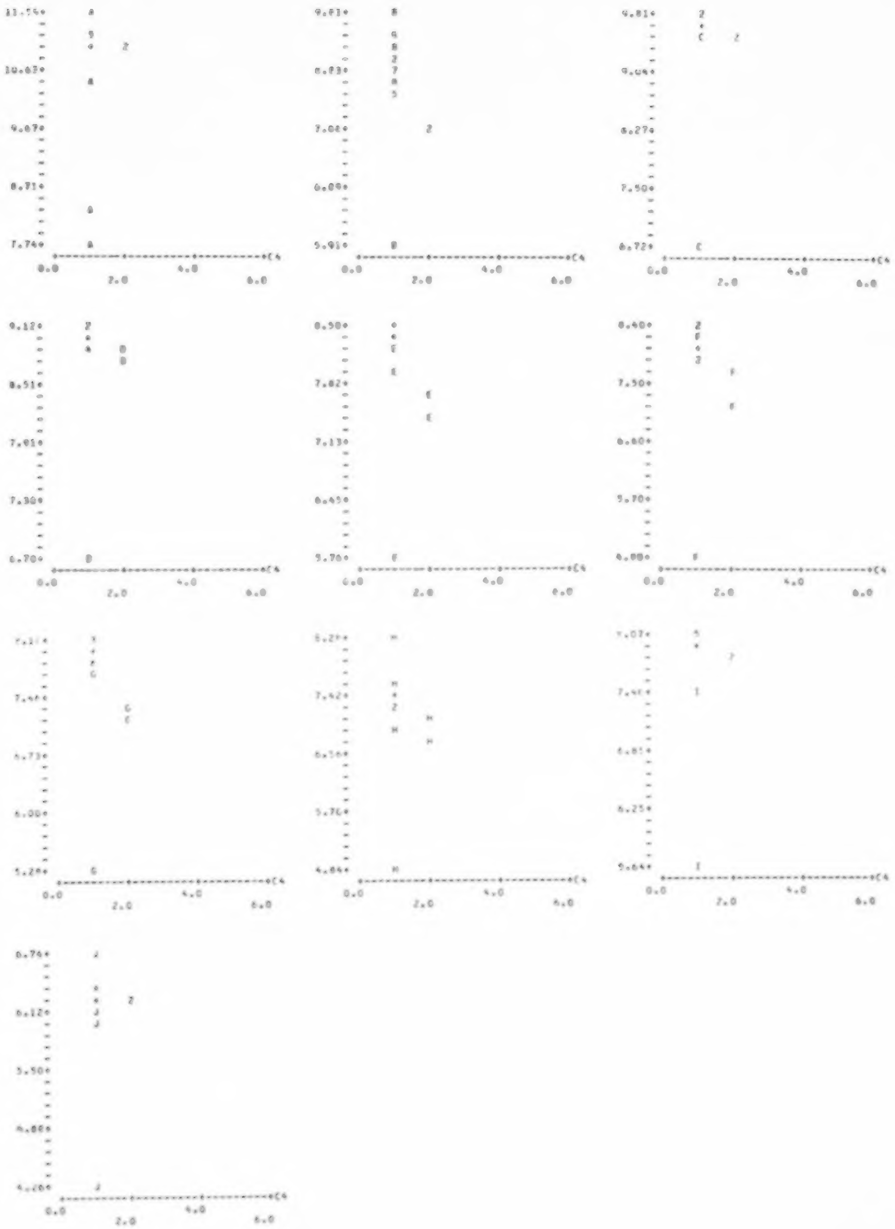

Figure C-7 Laboratory averages for log$_e$ transformed total residue data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J, respectively.

The low rank sums scored by both laboratories using the Total Residue Dried at 180°C method indicates that this method gives lower results than the Total Residue Dried at 103-105°C method. This conclusion is tenuous however as only two laboratories used the Total Residue Dried at 180°C method.

TABLE C-8-3 LABORATORY RANK SUMS FOR LOG_e TOTAL RESIDUE DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	200	15	97	33	79
2	216	18	88	34	103
4	10	19	195	37	101
7	114	20	165	40	185
8	134	21	187.5	42	191
9	244	23	144	43	167
10	109.5	25	150	46	151
12	179	28	232	48	25
13	175	29	149	49	38
14	231				

TABLE C-9-1. METHODS USED IN THE DETERMINATION OF VOLATILE RESIDUE

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Total Volatile & Fixed Residue at 550°C	24	11 to 264
2	Total Dissolved Volatiles	2	30 and 54
-1	Not Specified	1	74

TABLE C-9-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ VOLATILE RESIDUE DATA

Ordered Rank Sums	Method Code Number -1	1	2
11		4	
30			49
54			48
63		18	
-------*			
72		7	
74	34		
114		20	
116.5		25	
123		8	
124		29	
125		13	
139		1	
143		23	
143		43	
147		10	
152		21	
155		12	
162		15	
163		42	
180		37	
182.5		19	
186		28	
203		2	
208		46	
-------*			
221		40	
225		14	
264		9	

* Rank sums below 69 or above 211 are extreme scores.

The low ranks scored by both laboratories using the Total Dissolved Volatiles method indicates that this method gives lower results than the Total Volatile and Fixed Residue method. This conclusion is tenuous however as only two laboratories used the Total Dissolved Volatiles method. The "unspecified" method appears to give slightly lower results than the Total Volatile and Fixed Residue method.

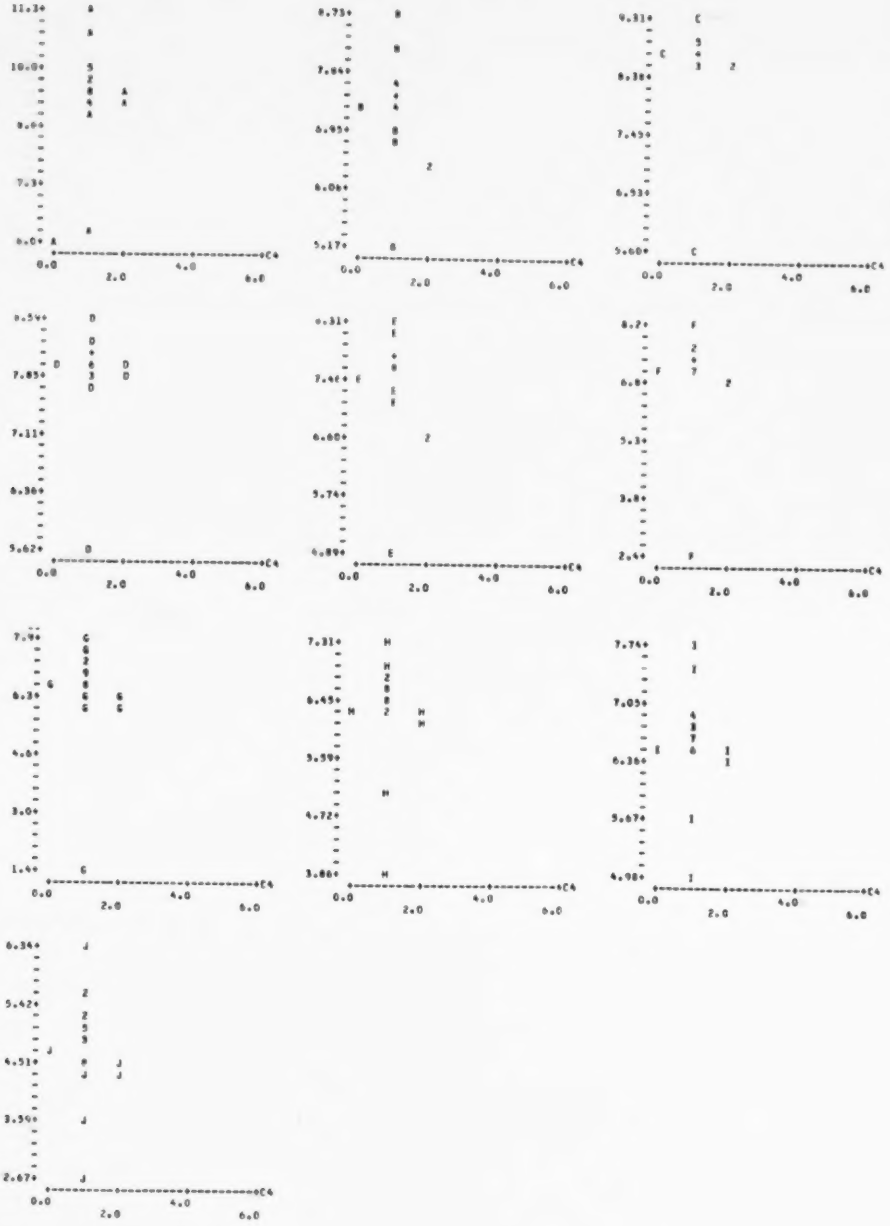

Figure C-8. Laboratory averages for $\log_e$ transformed volatile residue data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J, respectively. Method code number (-1) is plotted as a zero (0) in this figure.

TABLE C-9-3 LABORATORY RANK SUMS FOR LOG$_e$ VOLATILE RESIDUE DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	139	14	225	29	124
2	203	15	162	34	74
4	11	18	63	37	180
7	72	19	182.5	40	221
8	123	20	114	42	163
9	264	21	152	43	143
10	147	23	143	46	208
12	155	25	116.5	48	54
13	125	28	186	49	30

TABLE C-10-1 METHODS USED IN THE DETERMINATION OF ORGANIC NITROGEN

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Total Kjeldahl - Ammonia Nitrogen Titration	6	23 to 78
2	Total Kjeldahl - Ammonia Nitrogen Automated	11	35 to 163
3	Titration; not known if NH_3-N was subtracted	1	135

TABLE C-10-2 ORDERED LABORATORY RANK SUMS FOR LOG_e ORGANIC NITROGEN DATA

Ordered Rank Sums	Method Code Number 1	2	3
23	4		
35		49	
-----*			
66	42		
72	8		
72	28		
73	23		
74		21	
74		48	
78	37		
78		46	
82		43	
84		2	
133		34	
135			15
-----*			
153		29	
156		14	
159		10	
163		9	

* Rank sums below 49 or above 141 are extreme scores.

The Titration method appears to give lower results than the Automated method. Although this conclusion is tentative, the low rank sums scored by most of the laboratories using the Titration method are reasonably convincing evidence of a systematic difference between these methods. The laboratory using the Titration method, but where it was not known if ammonia nitrogen was subtracted, has a much larger rank sum than the other laboratories using the Titration method. If the ammonia nitrogen was subtracted than the difference between the Titration and Automated methods is not as apparent.

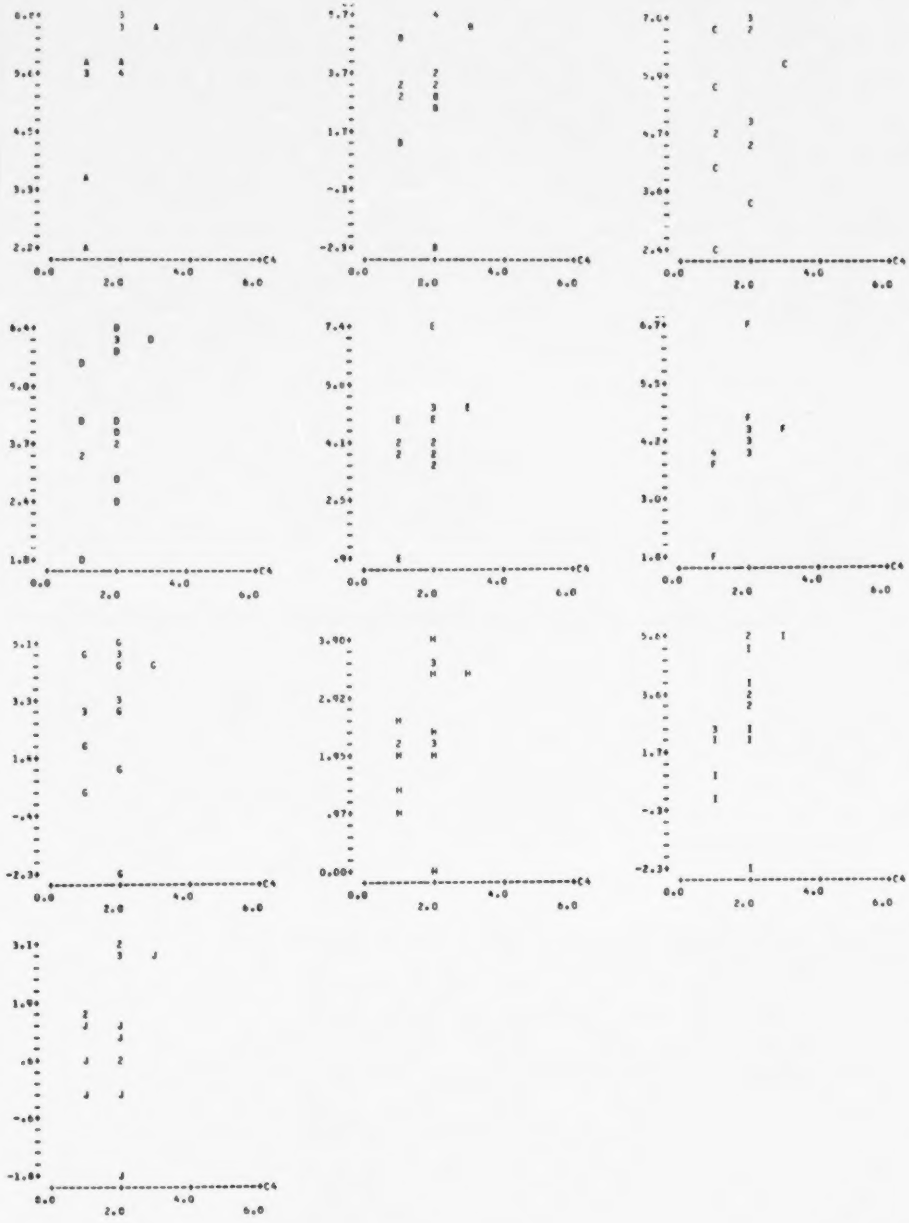

Figure C-9. Laboratory averages for $\log_e$ transformed organic nitrogen data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J, respectively.

TABLE C-10-3 LABORATORY RANK SUMS FOR LOG_e ORGANIC NITROGEN DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	84	15	135	37	78
4	23	21	74	42	66
8	72	23	73	43	82
9	163	28	72	46	78
10	159	29	153	48	74
14	156	34	133	49	35

TABLE C-11-1 METHODS USED IN THE DETERMINATION OF AMMONIA NITROGEN

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Titrimetric Following Distillation	6	29 to 113
2	Automated Colorimetric	12	17 to 178
3	Specific Electrode	5	74 to 238.5
4	Nesslerization Following Distillation	2	181.5 to 161.5

TABLE C-11-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ AMMONIA NITROGEN DATA

Ordered Rank Sums	Method Code Number 1	2	3	4
17		9		
29	4			
---------*				
67		50		
73	8			
74			54	
74	23			
92		33		
100	42			
106	37			
113	2			
116		46		
123		12		
143		7		
144		48		
150.5		49		
156.5		43		
160		29		
161			10	
161.5				25
169			14	
171		21		
178		18		
---------*				
201				28
232			51	
238.5			1	

* Rank sums below 64 or above 196 are extreme scores.

The Titrimetric Following Distillation method appears to give lower results than the other methods. The Specific Electrode and Nesslerization Following Distillation methods appear to yield similar results with both of these methods appearing to give higher results than the Automated Colorimetric method. One laboratory using the Specific Electrode method did have a fairly low rank sum, however this does not appreciably change the conclusions reached about this method.

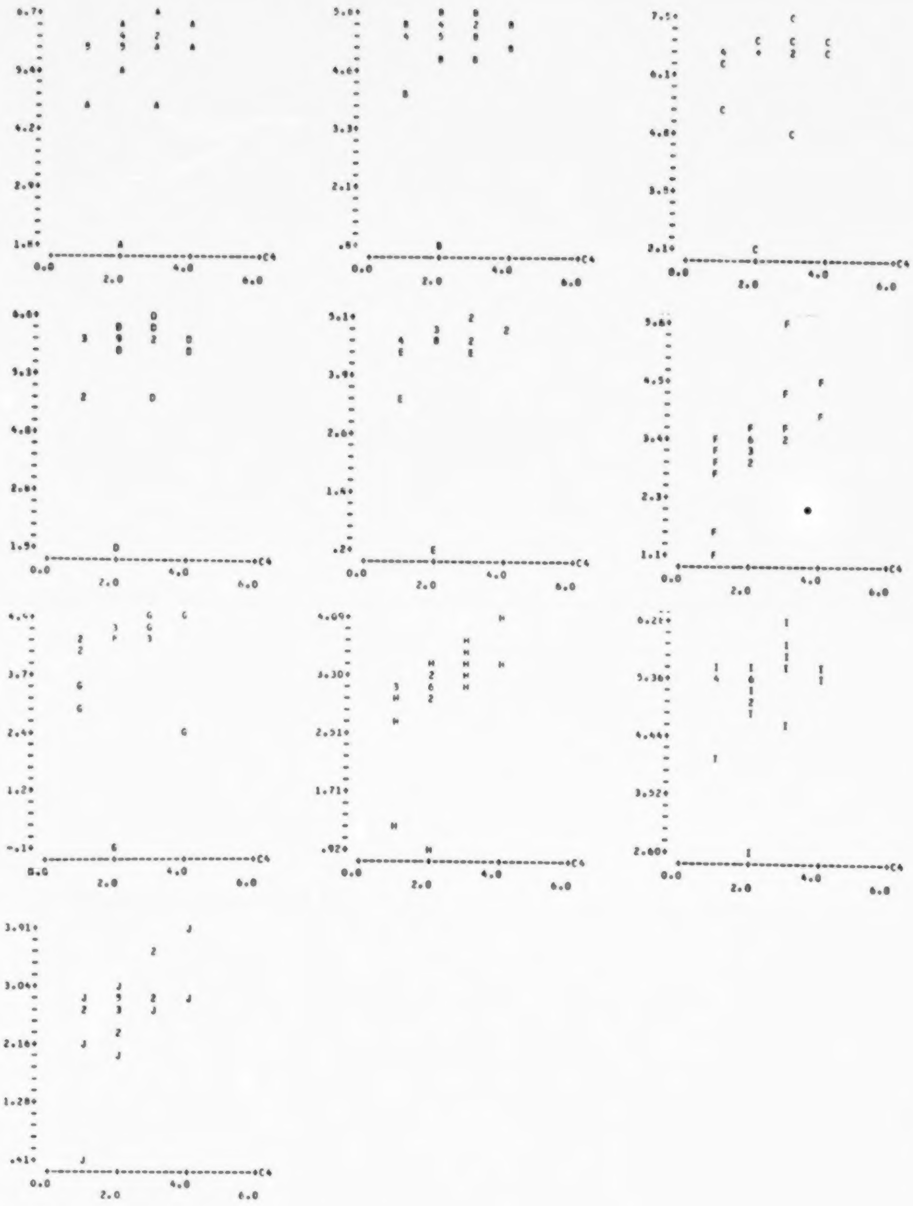

Figure C-10 Laboratory averages for $\log_e$ transformed ammonia nitrogen data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-11-3 LABORATORY RANK SUMS FOR LOG$_e$ AMMONIA NITROGEN DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	238.5	18	178	37	106
2	113	21	171	42	100
4	29	23	74	43	156.5
7	143	25	161.5	46	116
8	73	28	201	46	144
9	17	29	160	49	150.5
10	161	33	92	50	67
12	123	34	74	51	232
14	169				

TABLE C-12-1 METHODS USED IN THE DETERMINATION OF SULFATE

Method Code No.	Method	Number of labs	Rank sums scored by method
2	Gravimetric method with drying of residue	5	71.5 to 161
3	Turbidimetric	9	74.5 to 139
4	Methylthymol Blue - Automated	7	105 to 206.5
5	Turbidimetric - Automated	1	88
6	Barium Chloranilate - Colorimetric	1	144

TABLE C-12-2 ORDERED LABORATORY RANK SUMS FOR LOG_e SULFATE DATA

Ordered Rank Sums	Method Code Number				
	2	3	4	5	6
71.5	14				
74.5		19			
82.5		12			
85		37			
88				20	
94.5		42			
97	1				
98		46			
99		2			
105			10		
105.5			48		
115.5		18			
117	4				
124	51				
133		8			
139			49		
139		9			
141			29		
144					50
160			34		
161	28				
179.5			21		
206.5			43		

* Rank sums below 60 or above 180 are extreme scores.

The Automated Turbidimetric method appears to yield slightly lower results than the other methods, however this conclusion is very tenuous as only one laboratory used this method. The Gravimetric and Turbidimetric methods appear to yield similar results with both of these methods appearing to give lower results than Automated Methylthymol Blue and Barium Chloranilate methods which appear to yield similar results. The Barium Chloranilate method was performed by only a single laboratory however, therefore conclusions about this method are very tenuous. The variability of the Gravimetric method appears larger than for the Turbidimetric and Automated Methylthymol Blue methods but this conclusion is rather tenuous. As noted above, laboratory 14 used the Gravimetric method for samples A through F and the Turbidimetric for samples G through J, however this does not change the above conclusions.

TABLE C-12-3. LABORATORY RANK SUMS FOR LOG$_e$ SULFATE DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	97	18	115.5	42	94.5
2	99	19	74.5	43	206.5
4	117	20	88	46	98
8	133	21	179.5	48	105.5
9	139	28	161	49	139
10	105	29	141	50	144
12	82.5	34	160	51	124
14	71.5	37	85		

TABLE C-13-1 METHODS USED IN THE DETERMINATION OF TOTAL PHOSPHORUS

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Ascorbic Acid	18	15.5 to 223
2	Stannous Chloride	5	42.5 to 164

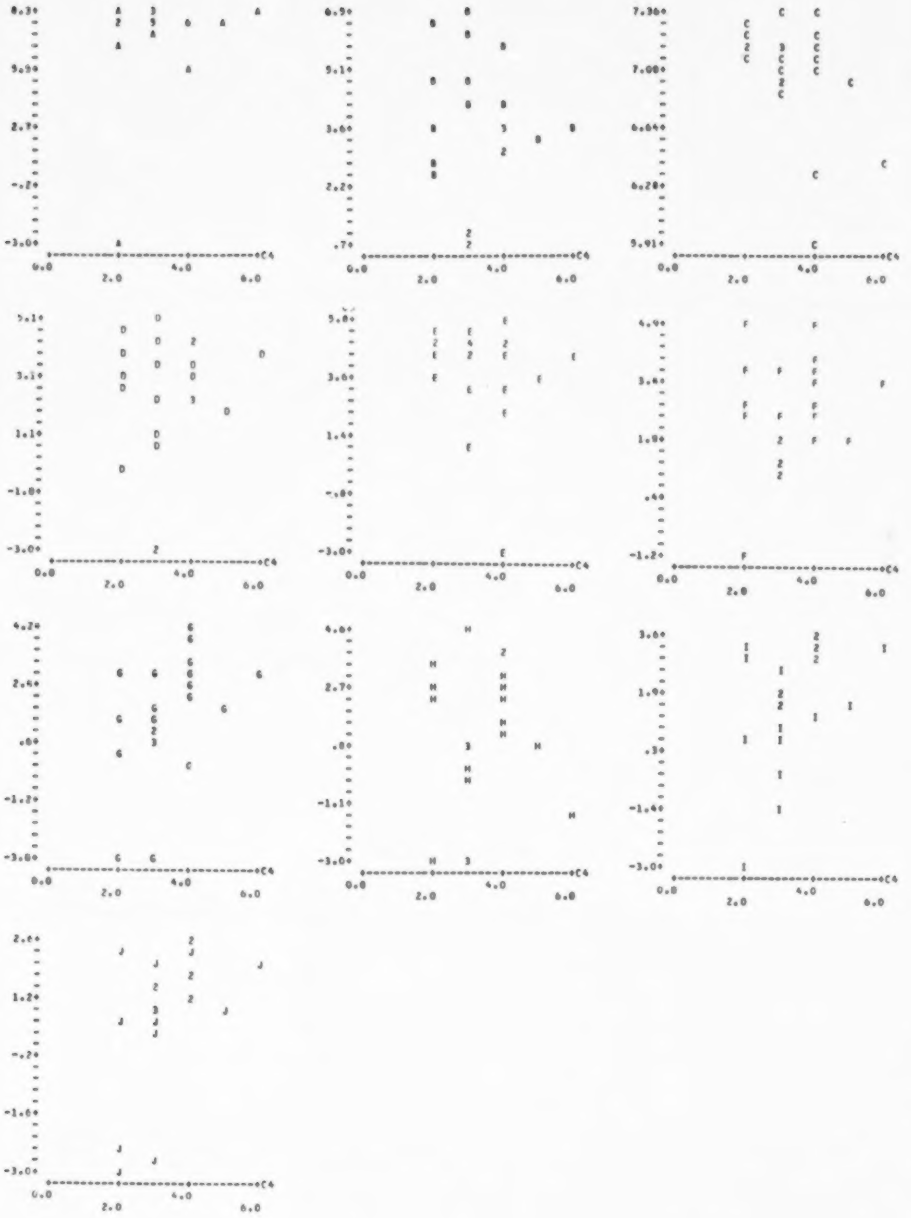

Figure C-11 Laboratory averages for $\log_e$ transformed sulfate data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-13-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ TOTAL PHOSPHORUS DATA

Ordered Rank Sums	Method Code Number 1	2
15.5	33	
24.5	49	
42.5		9
- - - - - *		
63.5	48	
74	21	
78		42
88		14
100	23	
103	37	
109.5	29	
110.5		8
111.5	19	
121.5	34	
131	10	
136	50	
145.5	25	
152	46	
164		43
166	2	
- - - - - *		
186.5	15	
205	28	
209	51	
223	4	

* Rank sums below 60 or above 180 are extreme scores.

Although both methods give reasonably similar results, the Stannous Chloride method appears to give slightly lower results than the Ascorbic Acid method. This conclusion is tenuous however as the results of these methods do overlap each other considerably.

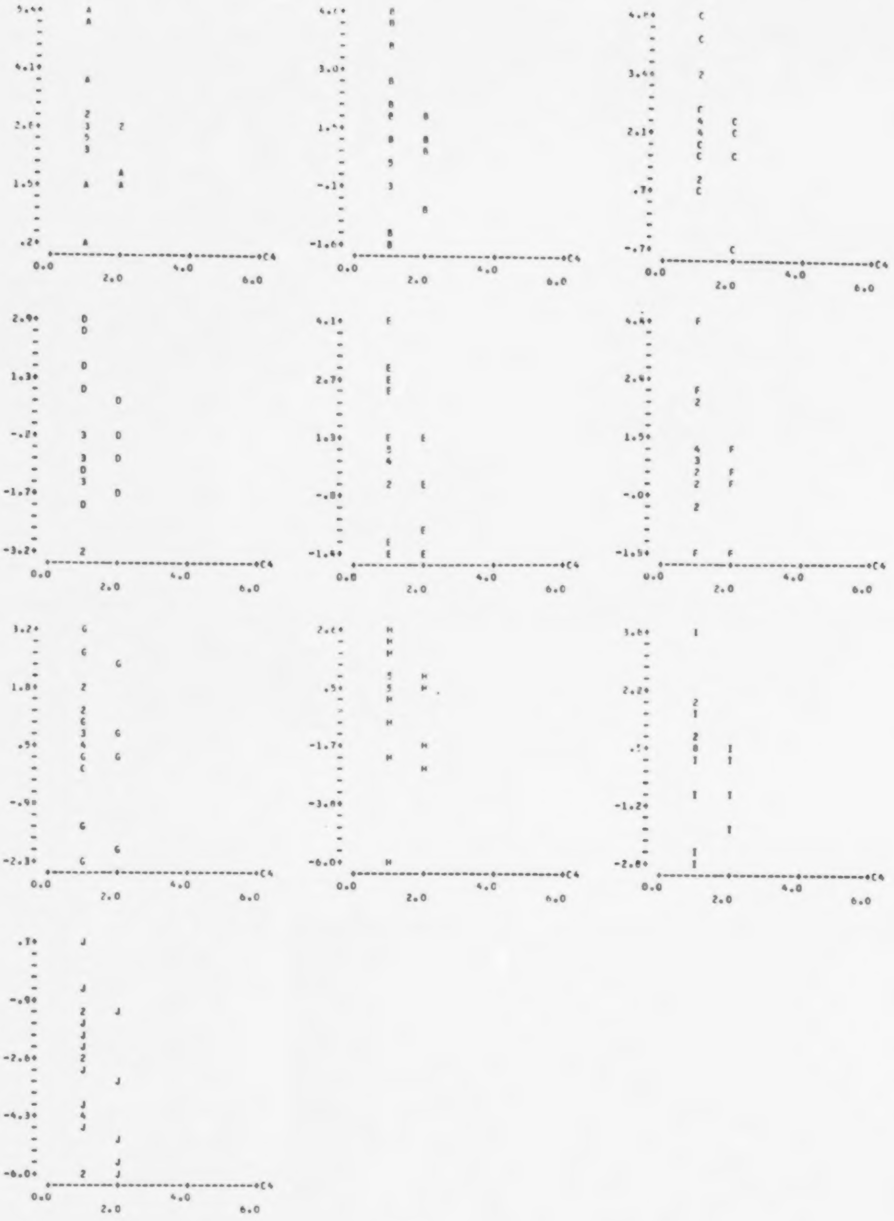

Figure C-12. Laboratory averages for $\log_e$ transformed total phosphorus data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-13-3 LABORATORY RANK SUMS FOR LOG_e TOTAL PHOSPHORUS DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	166	21	74	42	78
4	223	23	100	43	164
8	110.5	25	145.5	46	152
9	42.5	28	205	48	63.5
10	131	29	109.5	49	24.5
14	88	33	15.5	50	136
15	186.5	34	121.5	51	209
19	111.5	37	103		

TABLE C-14-1 METHODS USED IN THE DETERMINATION OF CHLORIDE

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Argentometric	4	80.5 to 200
2	Mercuric Nitrate	6	78 to 132
3	Potentiometric	2	103 and 105.5
4	Ferricyanide - Automated	13	70.5 to 195
5	Specific Ion Electrode	2	262 and 262

TABLE C-14-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ CHLORIDE DATA

Ordered Rank Sums	Method Code Number				
	1	2	3	4	5
70.5				29	
78		14			
80.5	19				
82		30			
95		37			
103			1		
105.5			4		
106.5		2			
114	43				
115.5				23	
121				46	
126.5				34	
131		20			
132		12			
135	8				
136.5				7	
139				49	
147				21	
157				50	
162				48	
164				28	
169.5				18	
190				42	
195				10	
200 --- *	25				
262					9
262					15

* Rank sums below 69 or above 211 are extreme scores.

The Mercuric Nitrate and Potentiometric methods appear to yield similar results with both of these methods appearing to give lower results than the other methods. The conclusions for the Potentiometric method is tenuous however as only two laboratories used this method. The Argentometric method and Automated Ferricyanide methods appear to give similar results. The variability of the Argentometric method appears to be relatively high. The two laboratories using the Specific Ion Electrode method had the two highest rank sum scores which indicates that this method gives higher results than the other methods. This conclusion is tenuous however as only two laboratories used this method.

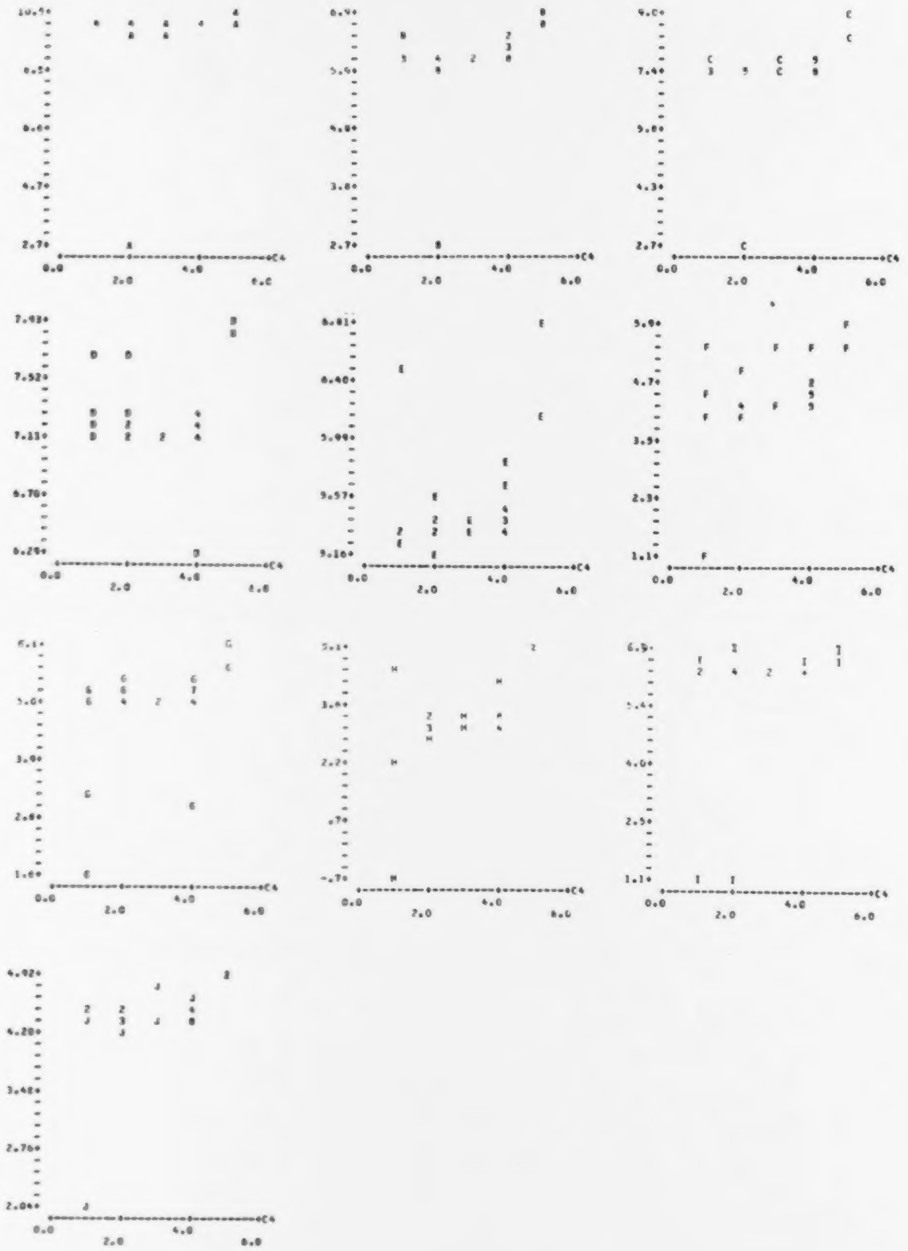

Figure C-13 Laboratory averages for $\log_e$ transformed chloride data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-14-3 LABORATORY RANK SUMS FOR $\log_e$ CHLORIDE DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	103	15	282	30	82
2	106.5	18	169.5	34	126.5
4	105.5	19	80.5	37	95
7	136.5	20	131	42	190
8	135	21	147	43	114
9	262	23	115.5	46	121
10	195	25	200	48	162
12	132	28	164	49	139
14	78	29	70.5	50	157

TABLE C-15-1 METHODS USED IN THE DETERMINATION OF ALKALINITY

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Potentiometric	14	41.5 to 238
2	Indicator (Colorimetric)	2	28.5 and 158.5
4	Automated - Colorimetric	1	89
5	Automated - pH	4	52.5 to 92
3	Not Specified	4	140 to 196

TABLE C-15-3. LABORATORY RANK SUMS FOR $\log_e$ ALKALINITY DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	171	14	117	34	89
2	184	15	213	42	147
3	175	19	152.5	43	92
4	238	20	183	46	158.5
7	41.5	21	178	48	52.5
8	28.5	23	84	49	87.5
9	196	28	140	50	97.5
10	84	29	64	51	179.5
12	97				

TABLE C-15-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ ALKALINITY DATA

Ordered	Method Code Number				
Rank Sums	1	2	3	4	5
28.5		8			
41.5	7				
52.5					48
------*					
64	29				
84	23				
84					10
87.5					49
89				34	
92					43
97	12				
97.5	50				
117	14				
140			28		
147			42		
152.5			19		
158.5		46			
171	1				
175	3				
178	21				
179.5	51				
183	20				
184	2				
196			9		
------*					
213	15				
238	4				

* Rank sums below 64 or above 196 are extreme scores.

The Automated Colorimetric and Automated pH methods and perhaps the Indicator method appear to yield similar results which are lower than the results of the other methods. The conclusion for the Automated Colorimetric method is quite tenuous however as only one laboratory used this method. Two laboratories used the Indicator method which makes conclusions about this method tenuous and additionally the variability of this method appears relatively large. The Potentiometric method and the "unspecified" method appear to give similar results. As noted above, laboratory 46 used the Indicator method for all samples except H and J and the Automated Colorimetric method for samples H and J, however this does not change the above conclusions.

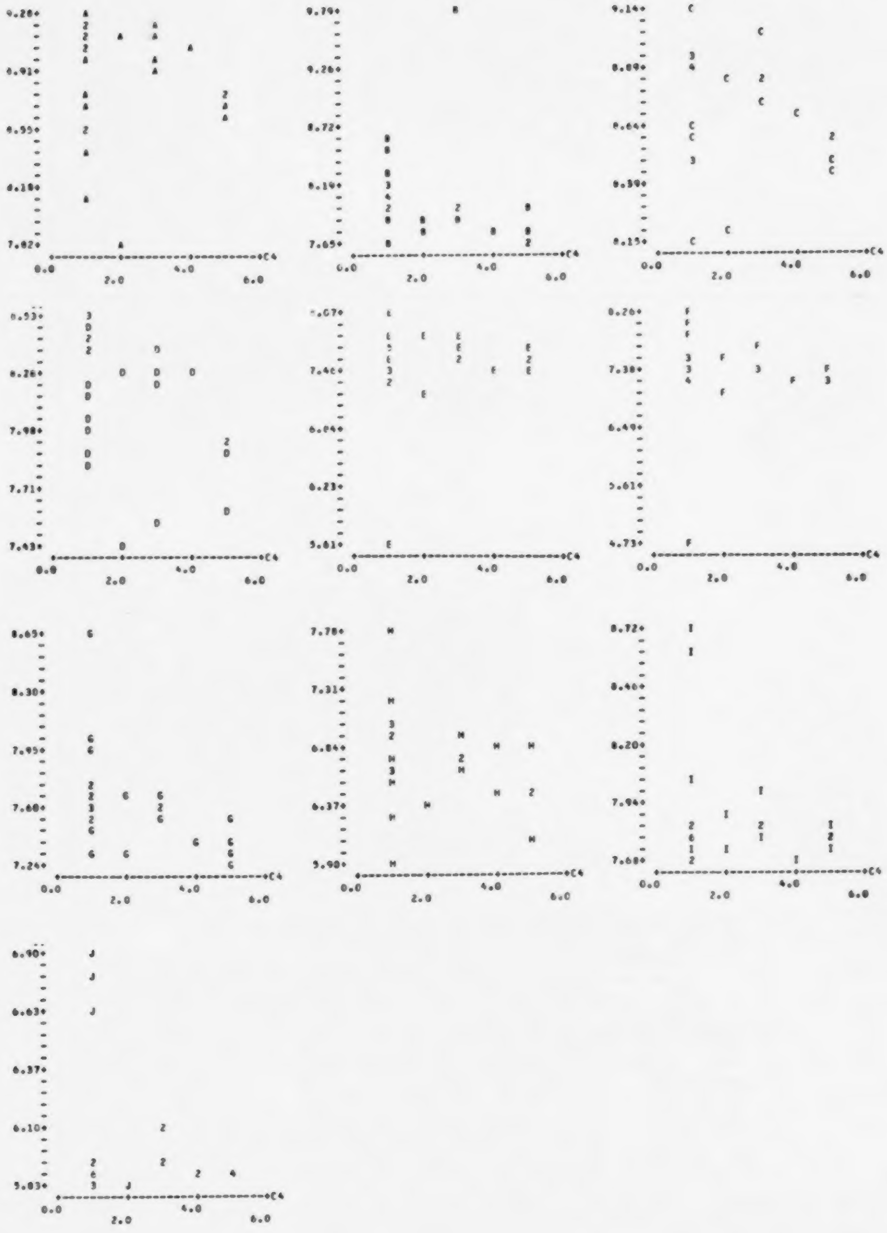

Figure C-14 Laboratory averages for $\log_e$ transformed alkalinity data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J, respectively.

TABLE C-16-1 METHODS USED IN THE DETERMINATION OF NITRATE NITROGEN

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Cadmium Reduction (NO_3)	12	27 to 195
2	Cadmium Reduction (NO_3 + NO_2)	4	68 to 133
3	Zinc Reduction	1	194
4	Nitrate Ion Electrode	2	51 and 216
5	Brucine	3	143 to 213
6	UAC - Griess Salzman Method	1	140

TABLE C-16-2 ORDERED LABORATORY RANK SUMS FOR LOG_e NITRATE NITROGEN DATA

Ordered Rank Sums	Method Code Number 1	2	3	4	5	6
27	25					
51				51		
--------*						
64	23					
68		50				
73.5	33					
76	34					
76	49					
82.5	2					
86	10					
97.5		29				
105.5	48					
112.5		21				
133		46				
140						18
143.5					12	
146	43					
151	9					
152	19					
157					37	
--------*						
194			28			
195	8					
213					42	
216				14		

* Rank sums below 60 or above 180 are extreme scores.

The Cadmium Reduction-Nitrate, Cadmium Reduction-Nitrate and Nitrite, and UAC-Griess Salzman methods appear to yield similar results which appear lower than the results obtained from the Zinc Reduction and Brucine methods which have similar results. The conclusions for the Zinc Reduction and UAC-Griess Salzman methods are quite tenuous however as each method was performed by only a single laboratory. The Nitrate Ion Electrode method appears to have a high variability as the two laboratories using this method had the second lowest and the highest rank sum scores. The high variability of this method makes any systematic difference comparisons with the other methods quite unclear.

TABLE C-16-3 LABORATORY RANK SUMS FOR LOG$_e$ NITRATE NITROGEN DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	82.5	21	112.5	42	213
8	195	23	64	43	146
9	151	25	27	46	133
10	86	28	194	48	105.5
12	143.5	29	97.5	49	76
14	216	33	73.5	50	68
18	140	34	76	51	51
19	152	37	157		

TABLE C-17-1 METHODS USED IN THE DETERMINATION OF SODIUM

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry (direct?)	19	23 to 260
2	Flame Photometric	6	132 to 238
4	A.A.S. - Graphite Furnace	1	52
5	Automated Flame Photometric	1	159.5
3	Not Specified	1	90

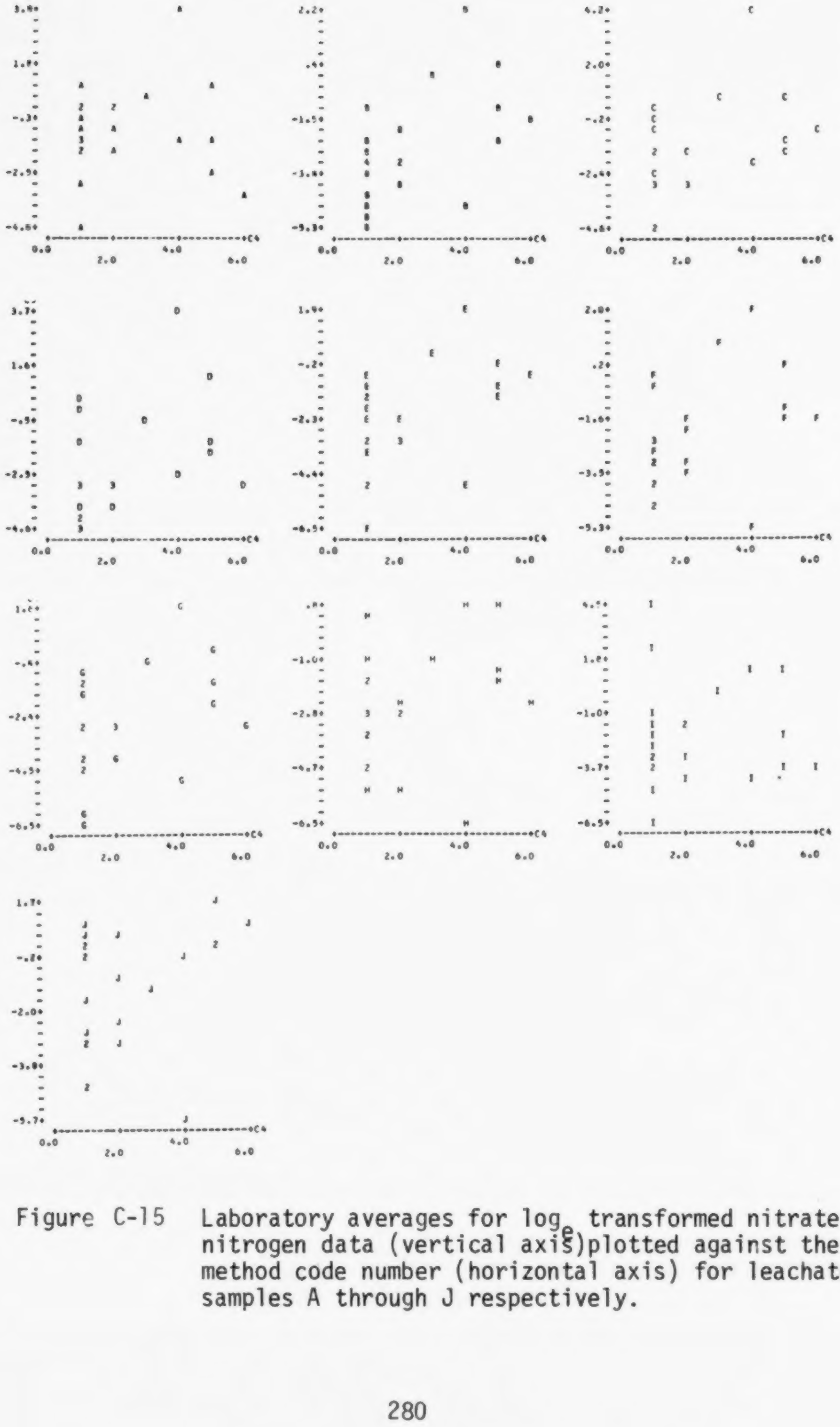

Figure C-15 Laboratory averages for $\log_e$ transformed nitrate nitrogen data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-17-2 ORDERED LABORATORY RANK SUMS FOR LOG_e SODIUM DATA

Ordered Rank Sums	Method Code Number 1	2	3	4	5
23	42				
52				25	
63	29				
66	34				
--------*					
80	7				
90			28		
95.5	19				
119.5	2				
120	8				
132		21			
132	30				
132.5	12				
133		50			
147		10			
153	18				
158.5	49				
159.5					23
162	43				
165	40				
176		4			
177.5	13				
190	46				
202.5	15				
205	48				
205.5		8			
--------*					
222	9				
238		37			
260	5				

* Rank sums below 71 or above 219 are extreme scores.

The results obtained by the A.A.S.-Graphite Furnace method appears to be lower than all other methods, however as only a single laboratory used this method this conclusion is very tenuous. The A.A.S. (direct?), Flame Photometric, Automated Flame Photometric and "unspecified" methods all appear to yield similar results. The conclusions for the Automated Flame Photometric and "unspecified" methods are very tenuous as each of these methods was performed by only a single laboratory.

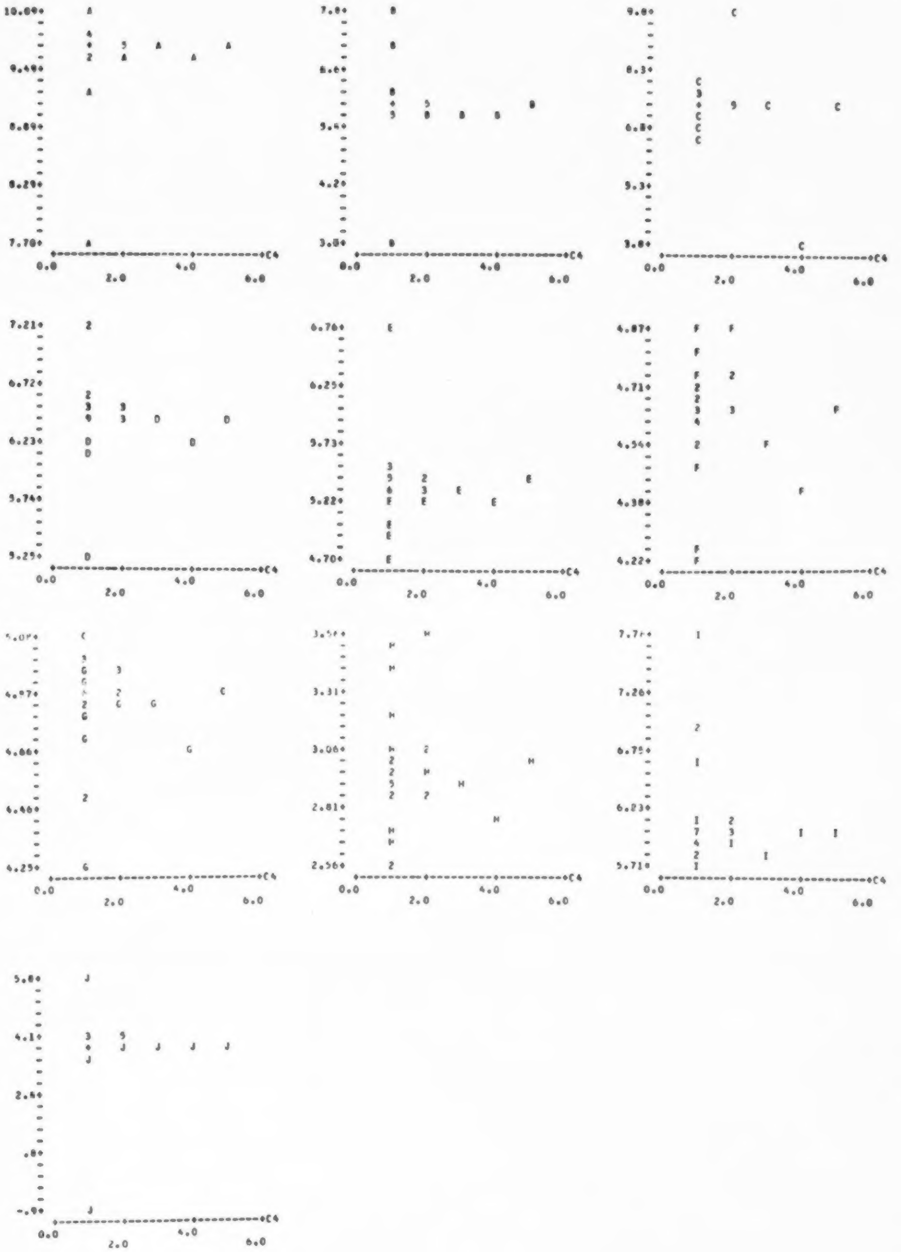

Figure C-16 Laboratory averages for $\log_e$ transformed sodium data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-17-3 LABORATORY RANK SUMS FOR LOG$_e$ SODIUM DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	119.5	15	202.5	34	66
4	176	18	153	37	238
5	280	19	95.5	40	165
6	120	21	132	42	23
7	80	23	159.5	43	162
8	205.5	25	52	46	190
9	222	28	90	48	205
10	147	29	63	49	158.5
12	132.5	30	132	50	133
13	177.5				

TABLE C-18-1 METHODS USED IN THE DETERMINATION OF POTASSIUM

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry (direct?)	19	61 to 265
2	Flame Photometric	7	18 to 285
5	Automated Flame Photometric	1	154
6	A.A.S. Flameless Emission	1	75
3	Not Specified	1	180

TABLE C-18-3 LABORATORY RANK SUMS FOR LOG$_e$ POTASSIUM DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	126	15	173	34	78.5
4	285	18	192	37	235
5	248	19	195.5	40	101
6	158	20	61	42	265
7	120	21	224	43	166.5
8	231.5	23	154	46	75
9	91	25	18	48	134
10	36	28	180	49	225
12	101	29	71	50	129
13	155.5	30	126.5		

TABLE C-18-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ POTASSIUM DATA

Ordered Rank Sums	Method Code Number				
	1	2	3	5	6
18		25			
36		10			
61	20				
71	29				
-------*					
75					46
78.5	34				
91	9				
101	40				
101	12				
120	7				
126	2				
126.5	30				
129		50			
134	48				
154				23	
155.5	13				
158	6				
160.5	43				
173	15				
180			28		
192	18				
195.5	19				
224		21			
225	49				
-------*					
231.5		8			
235		37			
248	5				
265	42				
285		4			

* Rank sums below 73 or above 227 are extreme scores.

The somewhat low rank sum scored by the laboratory using the A.A.S. Flameless Emission method indicates that this method gives lower results than the other methods. This conclusion is very tenuous however, as only one laboratory used this method. The A.A.S. (direct?), Flame Photometric, Automated Flame Photometric, and the "unspecified" methods all appear to give similar results. The conclusions for the Automated Flame Photometric, and "unspecified" methods are very tenuous as each method was performed by only one laboratory. The Flame Photometric method appears more variable than the A.A.S. (direct?) method.

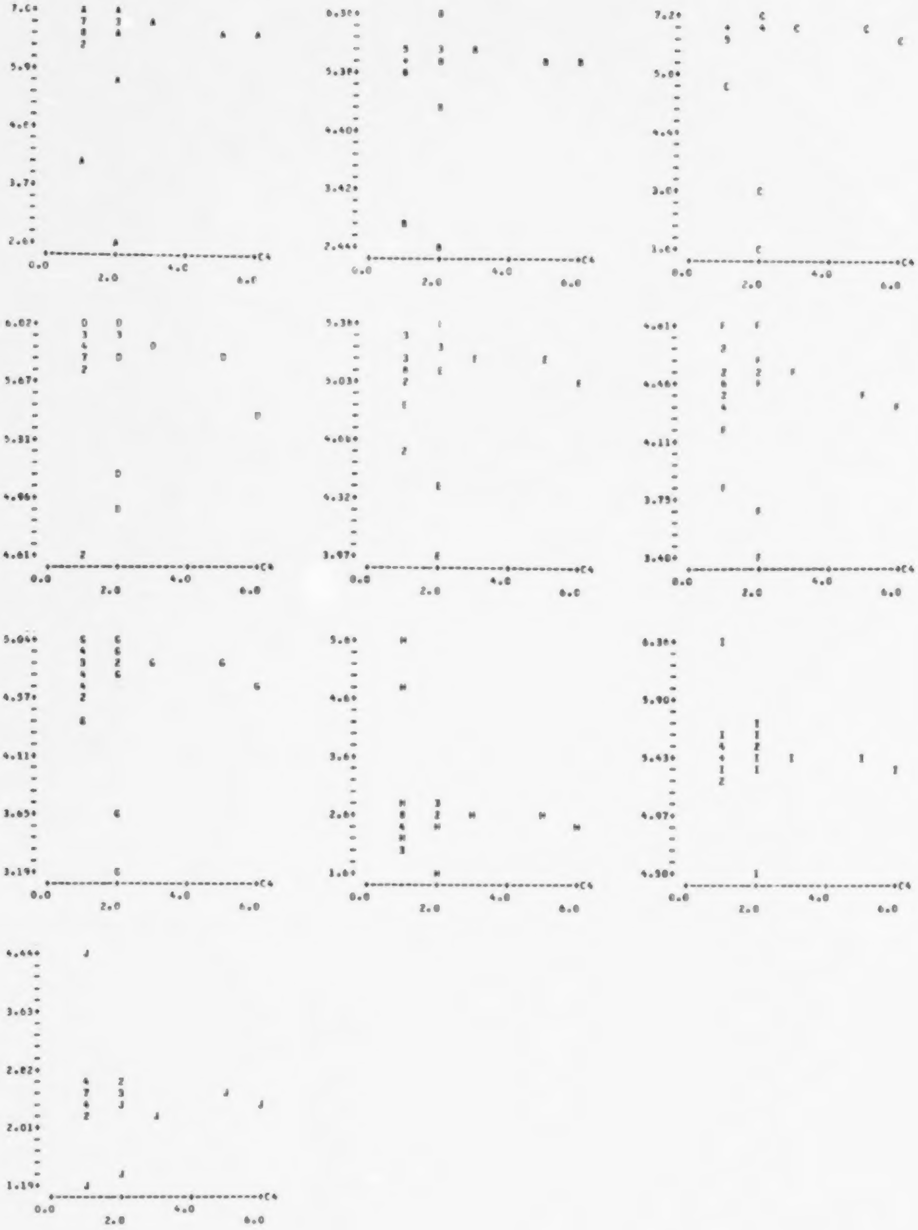

Figure C-17. Laboratory averages for $\log_e$ transformed potassium data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-19-1 METHODS USED IN THE DETERMINATION OF CALCIUM

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry (direct?)	23	40 to 259
2	A.A.S. - Graphite Furnace	2	203 and 280
3	EDTA Titration	3	73 to 97

TABLE C-19-2 ORDERED LABORATORY RANK SUMS FOR LOG_e CALCIUM DATA

Ordered Rank Sums	Method Code Number 1	2	3
40	9		
62	25		
68.5	29		
--------*			
73			8
74	37		
75	42		
94			21
97			10
100	7		
103	15		
121.5	30		
123	34		
125	50		
133.5	12		
140	28		
156	6		
164	40		
166	2		
169	20		
182	18		
194.5	48		
201	23		
202.5	49		
203		1	
206	46		
--------*			
247.5	19		
259	5		
280		4	

* Rank sums below 71 or above 219 are extreme scores.

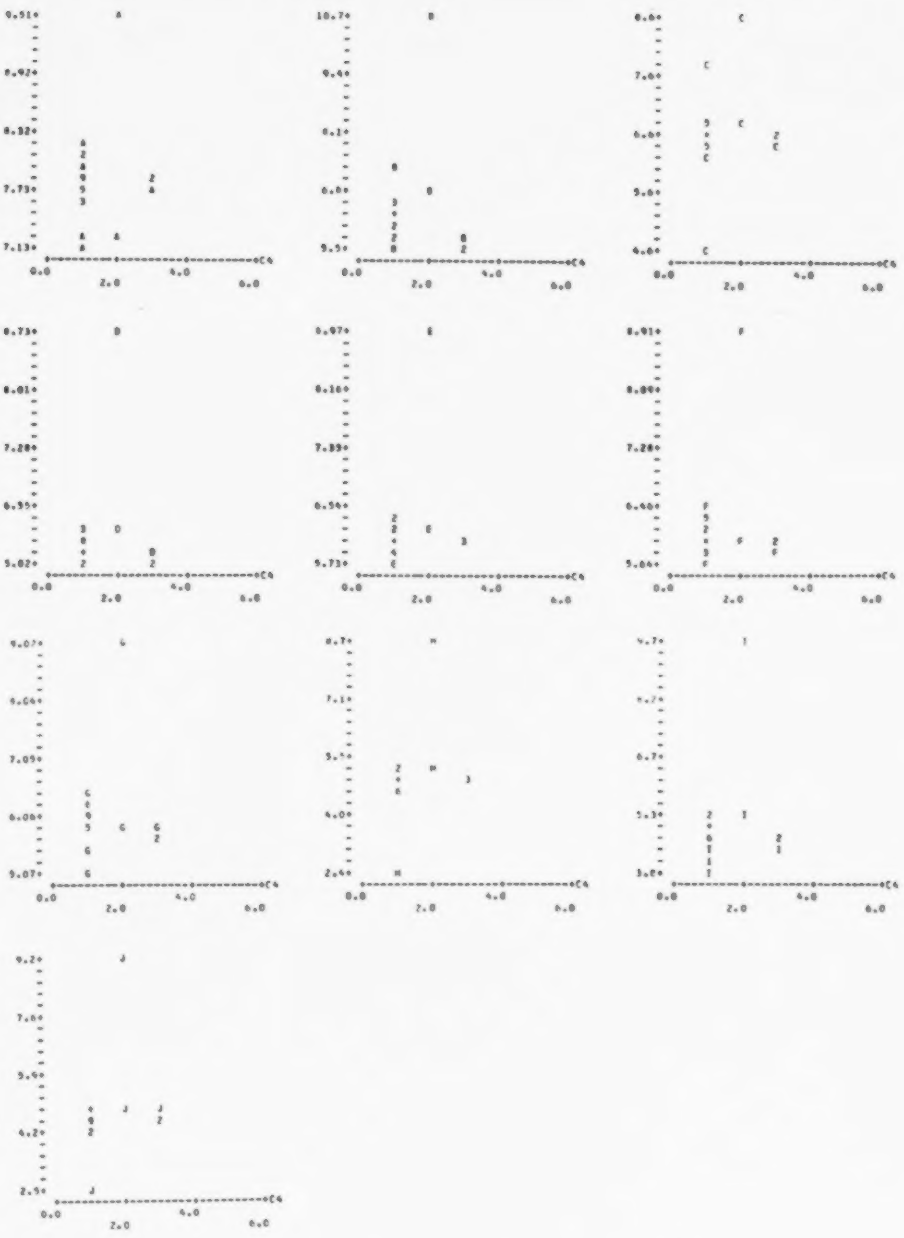

Figure C-18. Laboratory averages for $\log_e$ transformed calcium data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

The A.A.S.-Graphite Furnace method appears to give higher results than the other methods, however as only two laboratories used this method this conclusion is tenuous. The variability of the A.A.S.-Graphite Furnace method appears to be relatively large. The EDTA Titration method appears to give slightly lower results than the A.A.S. (direct?) method. The EDTA Titration method was used by only three laboratories which makes conclusions about this method tentative.

TABLE C-19-3 LABORATORY RANK SUMS FOR LOG_e CALCIUM DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	203	15	103	30	121.5
2	166	18	182	34	123
4	280	19	247.5	37	74
5	259	20	169	40	164
6	156	21	94	42	75
7	100	23	201	46	206
8	73	25	62	48	194.5
9	40	28	140	49	202.5
10	97	29	68.5	50	125
12	133.5				

TABLE C-20-1 METHODS USED IN THE DETERMINATION OF MAGNESIUM

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic A sorption Spectrophotometry (direct?)	25	35.5 to 238.5
2	EDTA Titration	2	88.5 and 163

TABLE C-20-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ MAGNESIUM DATA

Ordered Rank Sums	Method Code Number	
	1	2
35.5	25	
42	37	
43.5	29	
61.5	12	
---------*		
82	50	
88.5		10
108	34	
109	46	
126.5	23	
131	6	
135	28	
135	48	
135.5	2	
136.5	40	
138	42	
155	7	
158	30	
158.5	49	
163		21
175	20	
180.5	15	
193.5	18	
199	9	
202	8	
---------*		
219.5	19	
230	4	
238.5	5	

* Rank sums below 69 or above 211 are extreme scores.

The EDTA Titration and A.A.S. (direct?) methods appear to give similar results. The variability of the EDTA Titration method seems larger than the A.A.S. (direct?) method. These conclusions are tenuous however as only two laboratories used the EDTA Titration method.

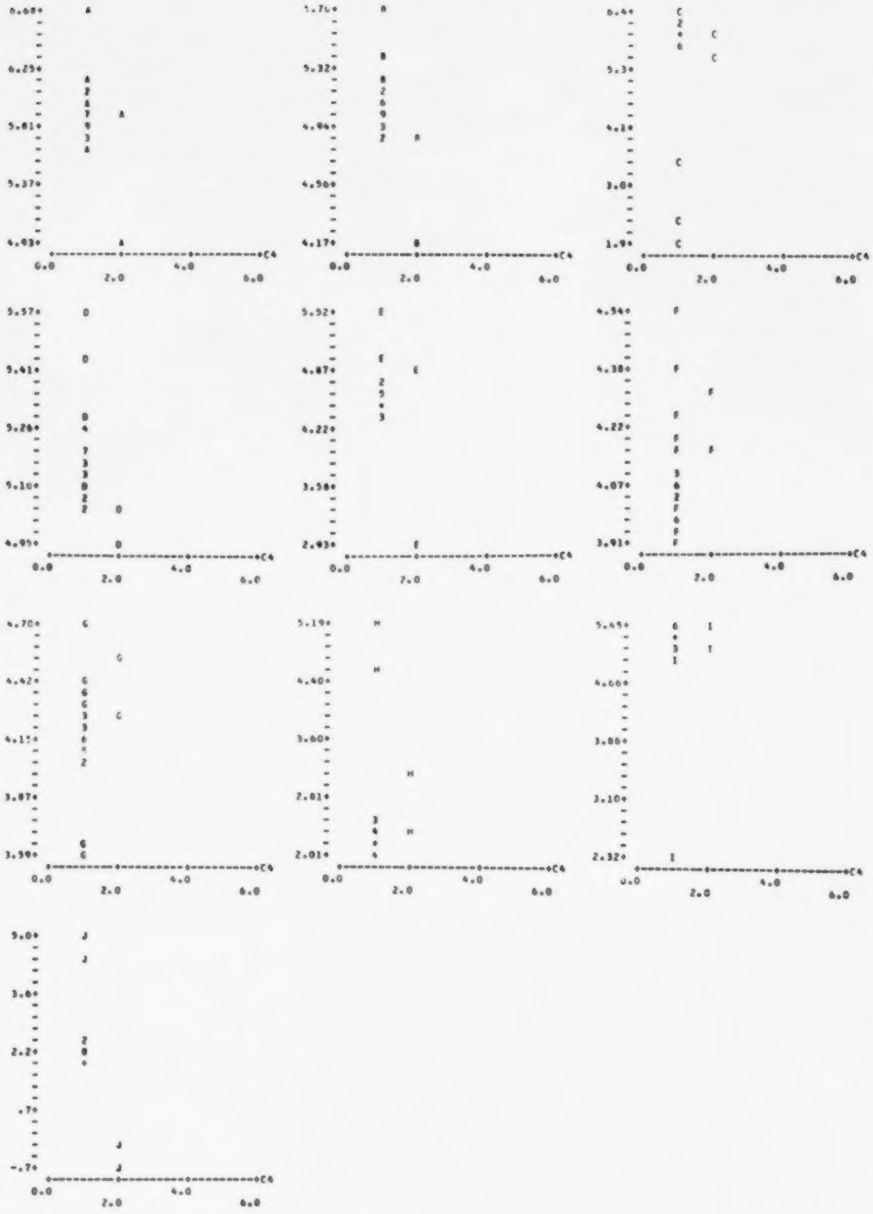

Figure C-19 Laboratory averages for $\log_e$ transformed magnesium data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-20-3. LABORATORY RANK SUMS FOR $\mathrm{LOG_e}$ MAGNESIUM DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	135.5	15	180.5	30	158
4	230	18	193.5	34	108
5	238.5	19	219.5	37	42
6	131	20	175	40	136.5
7	155	21	163	42	138
8	202	23	126.5	46	109
9	199	25	35.5	48	135
10	88.5	28	135	49	158.5
12	61.5	29	43.5	50	82

TABLE C-21-1 METHODS USED IN THE DETERMINATION OF BARIUM

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry (NO_2 - C_2H_2 Flame)	6	44 to 155
2	A.A.S. - flame not mentioned	11	21 to 167
3	Flame Emission (NO_2 - C_2H_2 Flame)	1	150

The A.A.S. (NO_2-C_2H_2 Flame) method and the A.A.S. (Unspecified Flame) method appear to give similar results. The high rank sum scored by the laboratory using the Flame Emission (NO_2-C_2H_2 Flame) method indicates that this method gives higher results than the other methods. This conclusion is very tenuous however as only one laboratory used the Flame Emission method.

TABLE C-21-2 ORDERED LABORATORY RANK SUMS FOR LOG_e BARIUM DATA

Ordered Rank Sums	Method Code Number		
	1	2	3
21		7	
27		37	
44	10		
--------*			
62		19	
68		28	
70	30		
72	49		
82		21	
94	2		
94.5		6	
107		34	
111		48	
115.5		29	
121	5		
--------*			
149		42	
150			23
155	4		
167		18	

* Rank sums below 49 or above 141 are extreme scores.

TABLE C-21-3 LABORATORY RANK SUMS FOR LOG_e BARIUM DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	94	18	167	30	70
4	155	19	62	34	107
5	121	21	82	37	27
6	94.5	23	150	42	149
7	21	28	68	48	111
10	44	29	115.5	49	72

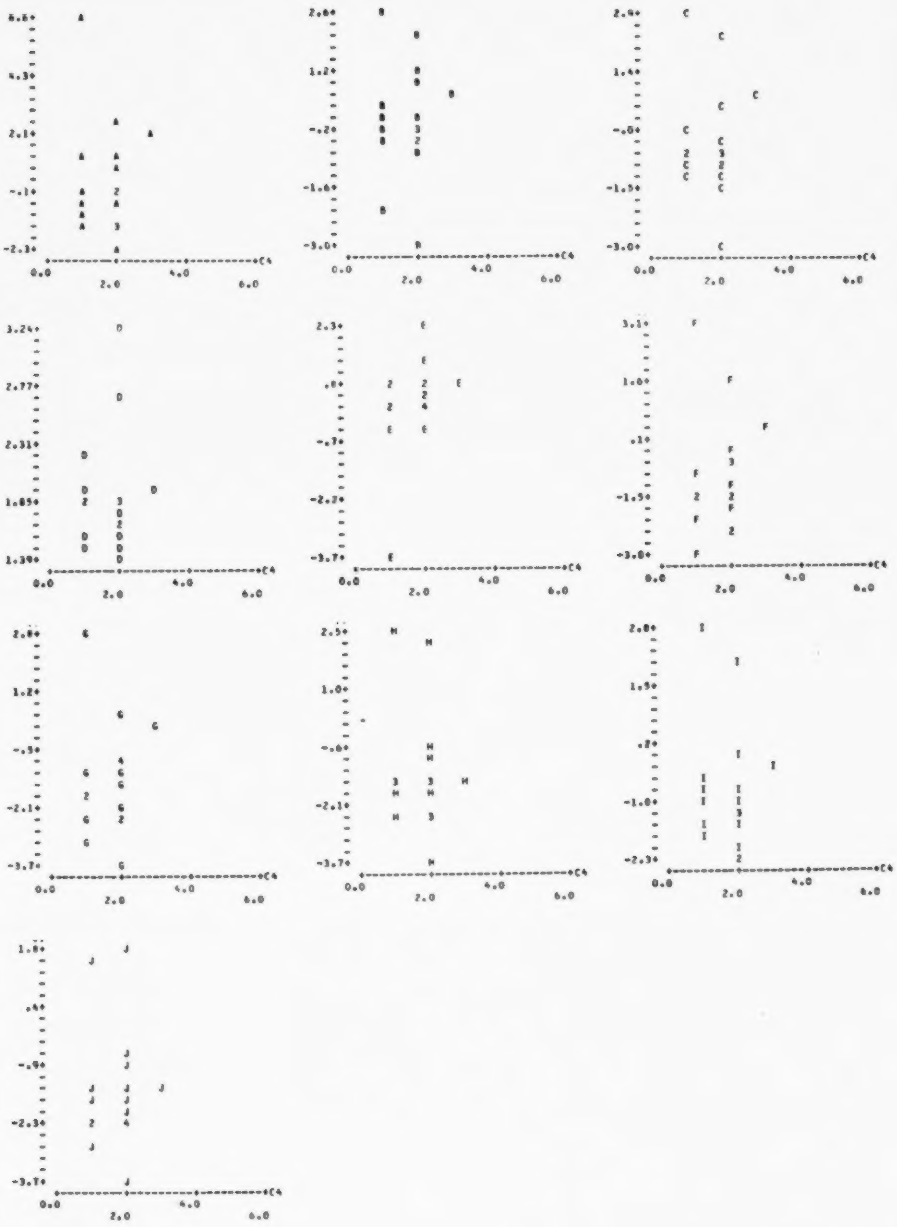

Figure C-20 Laboratory averages for $\log_e$ transformed barium data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-22-1 METHODS USED IN THE DETERMINATION OF IRON

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Colorimetric (Phenanthroline and Automated Bipyridine)	2	80.5 and 230
2	Atomic Absorption Spectrophotometry (direct?)	26	39 to 271

TABLE C-22-2 ORDERED LABORATORY RANK SUMS FOR LOG_e IRON DATA

Ordered Rank Sums	Method Code Number 1	2
39		34
46		18
50		25
58		9
---------*		
80.5	10	
82		7
92		29
94		20
95		28
110		4
125.5		13
142.5		50
148		15
151		42
155		2
165		46
171		40
174		21
175		19
177		8
180		30
183.5		6
214		49
215		5
218		12
218		23
---------*		
230	48	
271		37

* Rank sums below 71 or above 219 are extreme scores.

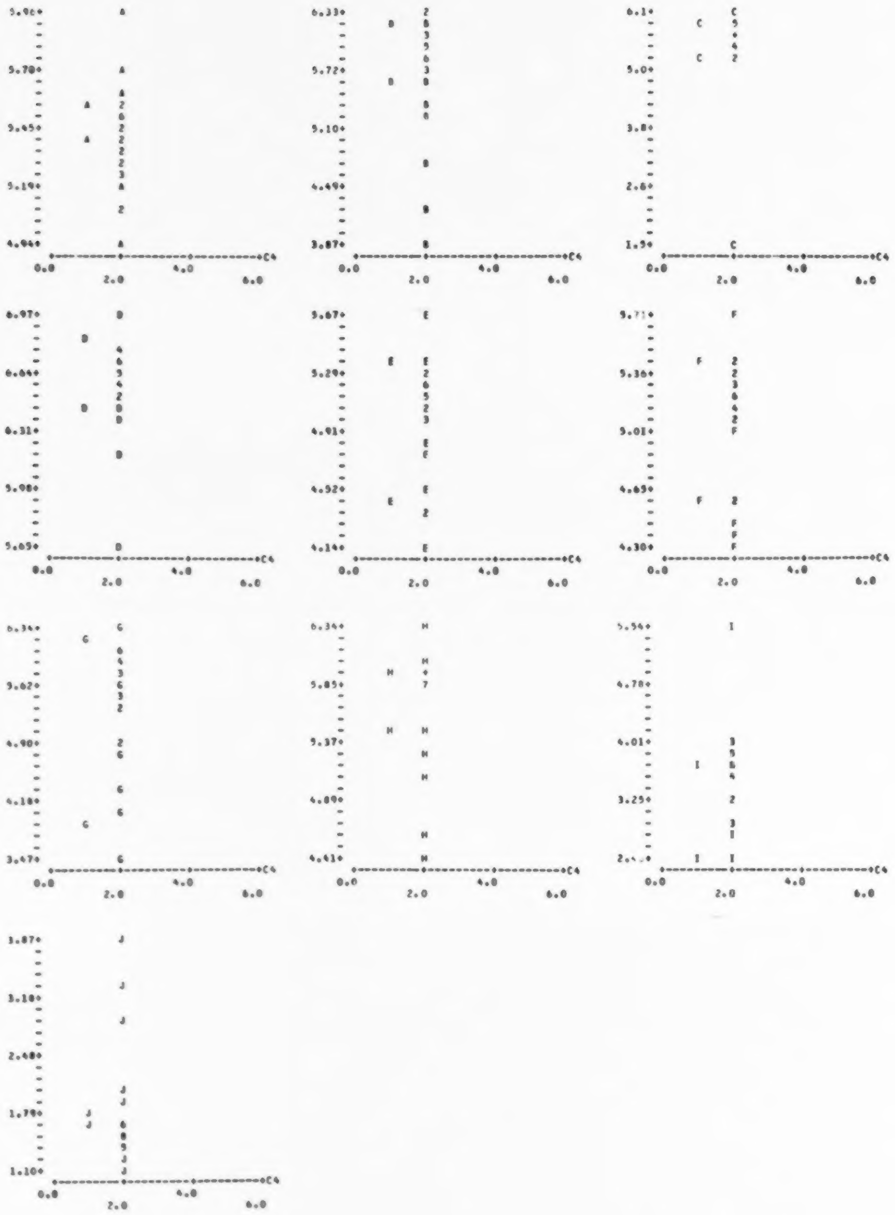

Figure C-21. Laboratory averages for $\log_e$ transformed iron data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-22-3. LABORATORY RANK SUMS FOR LOG$_e$ IRON DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	155	15	148	34	39
4	110	18	46	37	271
5	215	19	175	40	171
6	183.5	20	94	42	151
7	82	21	174	46	165
8	177	23	218	48	230
9	58	25	50	49	214
10	80.5	28	95	50	142.5
12	218	29	92		
13	125.5	30	180		

TABLE C-23-1 METHODS USED IN THE DETERMINATION OF ZINC

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry - Direct Aspiration	4	36 to 194
2	A.A.S. - (direct?)	23	14.5 to 265
3	A.A.S. - Graphite Furnace	2	209.5 and 290

TABLE C-23-3 LABORATORY RANK SUMS FOR LOG$_e$ ZINC DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	209.5	13	133.5	30	162
2	149	15	265	34	95
4	290	18	61.5	37	141
5	243.5	19	150	40	217
6	165.5	20	117	42	137
7	78	21	164	46	202.5
8	172	23	147.5	48	166.5
9	14.5	25	36	49	194
10	87.5	28	138	50	154
12	173	29	86		

TABLE C-23-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ ZINC DATA

Ordered Rank Sums	Method Code Number 1	2	3
14.5		9	
36	25		
61.5		18	
--------*			
78		7	
86		29	
87.5		10	
95		34	
117		20	
133.5		13	
137		42	
138		28	
141		37	
147.5		23	
149		2	
150		19	
154	50		
162		30	
164		21	
165.5		6	
166.5	48		
172		8	
173		12	
194	49		
202.5		46	
209.5			1
217		40	
--------*			
243.5		5	
265		15	
290			3

* Rank sums below 73 or above 227 are extreme scores.

The A.A.S.-Direct Aspiration and A.A.S. (direct?) methods appear to give similar results. The A.A.S.-Graphite Furnace method appears to give higher results than the other methods and additionally the variability of this method appears relatively large. The conclusions reached for the A.A.S. graphite furnace method are tenuous however as only two laboratories used this method.

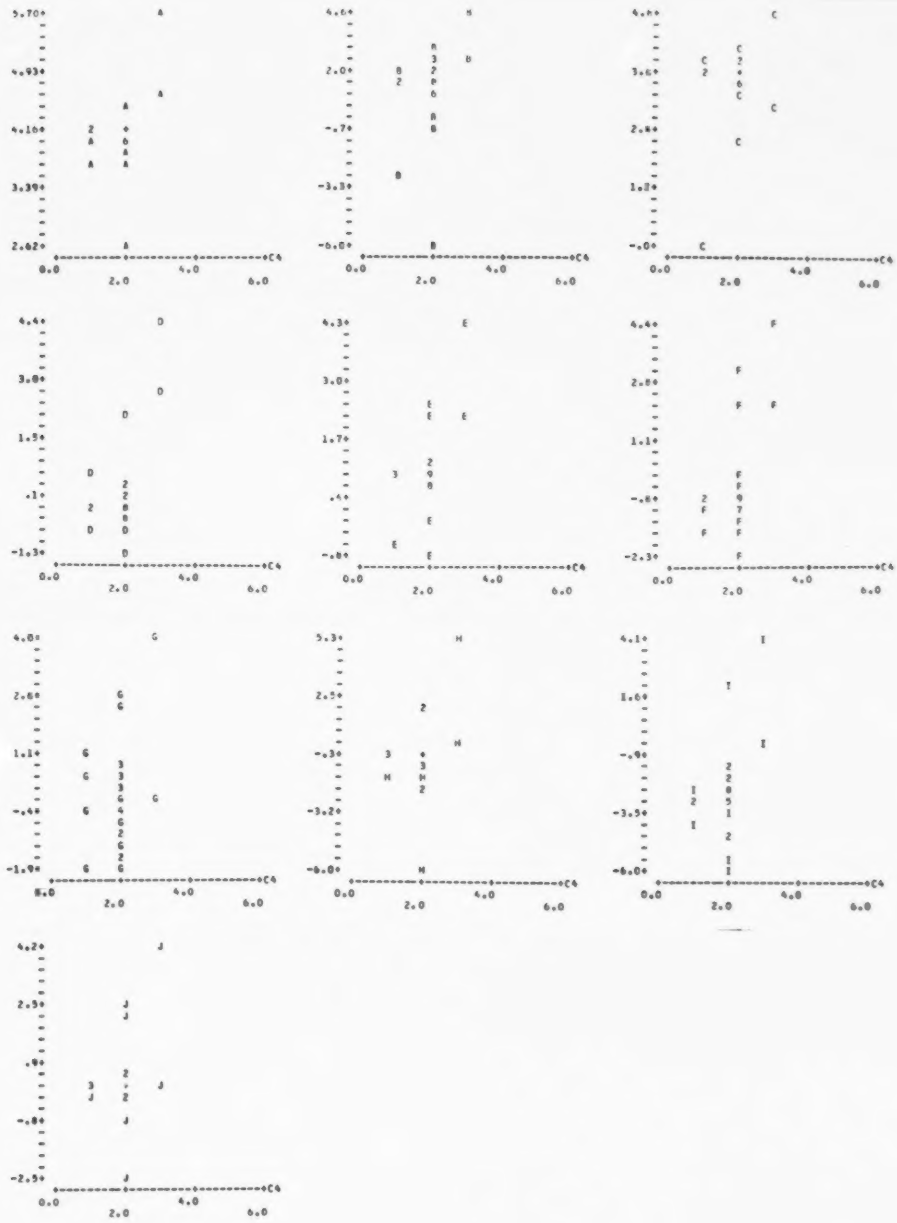

Figure C-22. Laboratory averages for $\log_e$ transformed zinc data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-24-1 METHODS USED IN THE DETERMINATION OF LEAD

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry - Direct Aspiration	4	92 to 180
2	A.A.S. - (direct?)	16	61 to 268
3	A.A.S. - Boat	1	77
4	A.A.S. - Graphite Furnace	6	42 to 119

The A.A.S.-Graphite Furnace method appears to give lower results than the A.A.S.-Direct Aspiration and A.A.S. (direct?) methods. The low rank sums scored by most of the laboratories using the A.A.S.-Graphite Furnace method is reasonably convincing evidence of a systematic difference between these methods. The somewhat low rank sum scored by the laboratory using the A.A.S.-Boat method indicates that this method also gives lower results than the A.A.S.-Direct Aspiration and A.A.S. (direct?) methods. The A.A.S.-Boat and A.A.S.-Graphite Furnace methods appear to give similar results. The conclusions for the A.A.S.-Boat method are very tenuous as only one laboratory used this method. The A.A.S.-Direct Aspiration and A.A.S. (direct?) methods appear to give similar results. As noted above, laboratory 23 used the A.A.S.-Direct Aspiration method for samples A through H and the A.A.S. (direct?) method for samples I and J, however this does not change the above conclusions.

TABLE C-24-2 ORDERED LABORATORY RANK SUMS FOR LOG_e LEAD DATA

Ordered Rank Sums	Method Code Number			
	1	2	3	4
42				8
51				42
61		10		
67.5				25
67.5				5
--------*				
76				40
77			7	
92	50			
104.5		2		
114		19		
114.5		6		
119				4
122		2		
147	23			
151		34		
163.5	49			
176		46		
180	48			
186.5		29		
190		18		
191.5		13		
196		30		
197		37		
198.5		28		
210		21		
--------*				
217		15		
268		20		

* Rank sums below 69 or above 211 are extreme scores.

TABLE C-24-3 . LABORATORY RANK SUMS FOR LOG_e LEAD DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	104.5	15	217	30	196
4	119	18	190	34	151
5	67.5	19	114	37	197
6	114.5	20	268	40	76
7	77	21	210	42	51
8	42	23	147	46	176
10	61	25	67.5	48	180
12	122	28	198.5	49	163.5
13	191.5	29	186.5	50	92

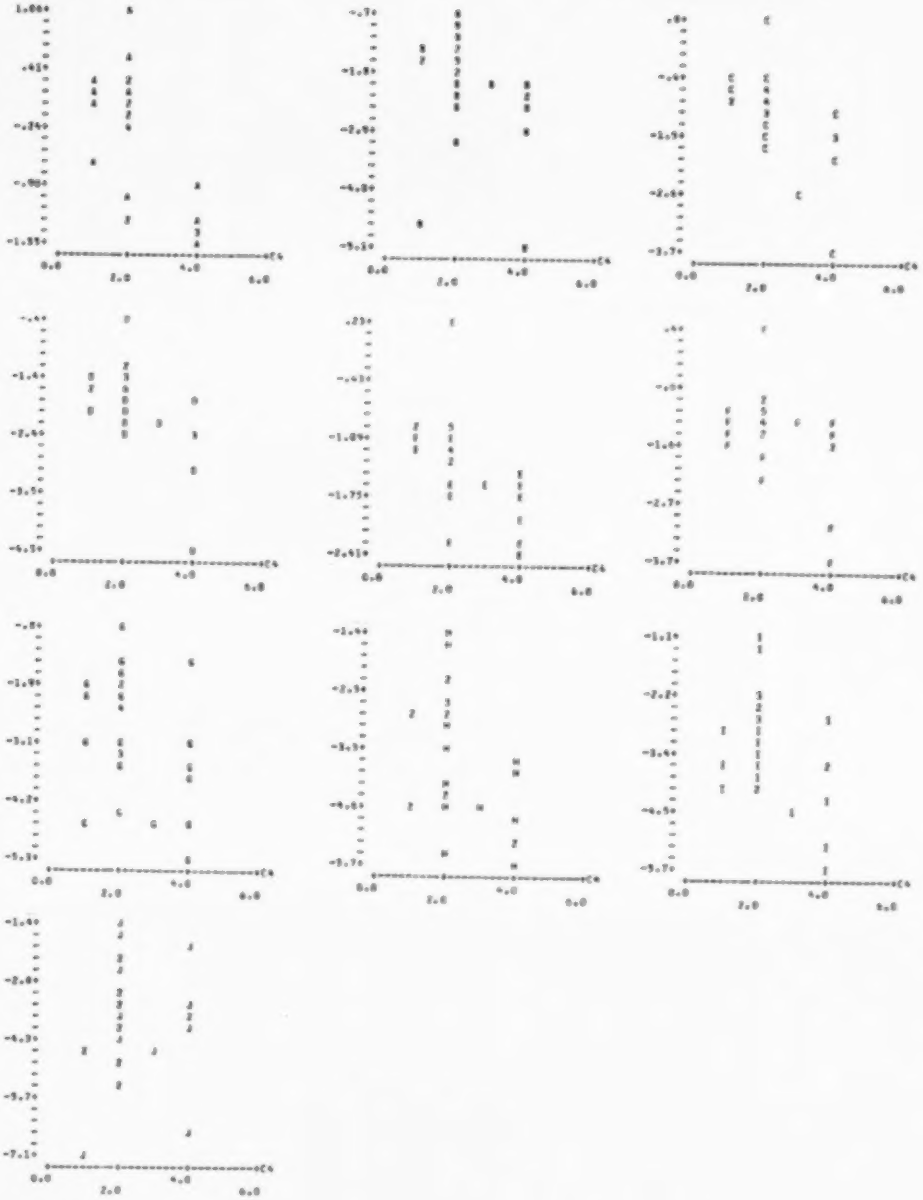

Figure C-23. Laboratory averages for $\log_e$ transformed lead data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-25-1 METHODS USED IN THE DETERMINATION OF CHROMIUM

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry -Direct Aspiration	6	45 to 165
2	A.A.S. (direct?)	18	36 to 275
3	A.A.S. Flameless - Graphite Furnace	4	61 to 251

TABLE C-25-3 LABORATORY RANK SUMS FOR LOG$_e$ CHROMIUM DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	126.5	15	165	30	166
4	251	18	197.5	34	224
5	61	19	121.5	37	275
6	84	20	163	40	65
7	65	21	123	42	90
8	247	23	174	46	206
9	36	25	45	48	147
10	113.5	28	129	49	143
12	162	29	148.5	50	73.5
13	258				

TABLE C-25-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ CHROMIUM DATA

Ordered Rank Sums	Method Code Number 1	2	3
38		9	
45	25		
61			5
65		40	
65		7	
---------*			
73.5	50		
84		6	
90			42
113.5			10
121.5		19	
123	21		
126.5		2	
129		28	
143	49		
147	48		
148.5		29	
162		12	
163		20	
165	15		
166		30	
174		23	
197.5		18	
206		46	
---------*			
224		34	
247		8	
251			4
258		13	
275		37	

* Rank sums below 71 or above 219 are extreme scores.

The A.A.S. Flameless-Graphite Furnace method appears to give similar or perhaps slightly lower results than the A.A.S.-Direct Aspiration and A.A.S. (direct?) methods. The somewhat high rank sum scored by one of the laboratories using the Graphite Furnace method makes the conclusions about this method very tenuous however. The variability of the A.A.S. Flameless-Graphite Furnace method is perhaps higher than these other methods. The A.A.S.-Direct Aspiration and A.A.S. (direct?) methods appear to give similar results.

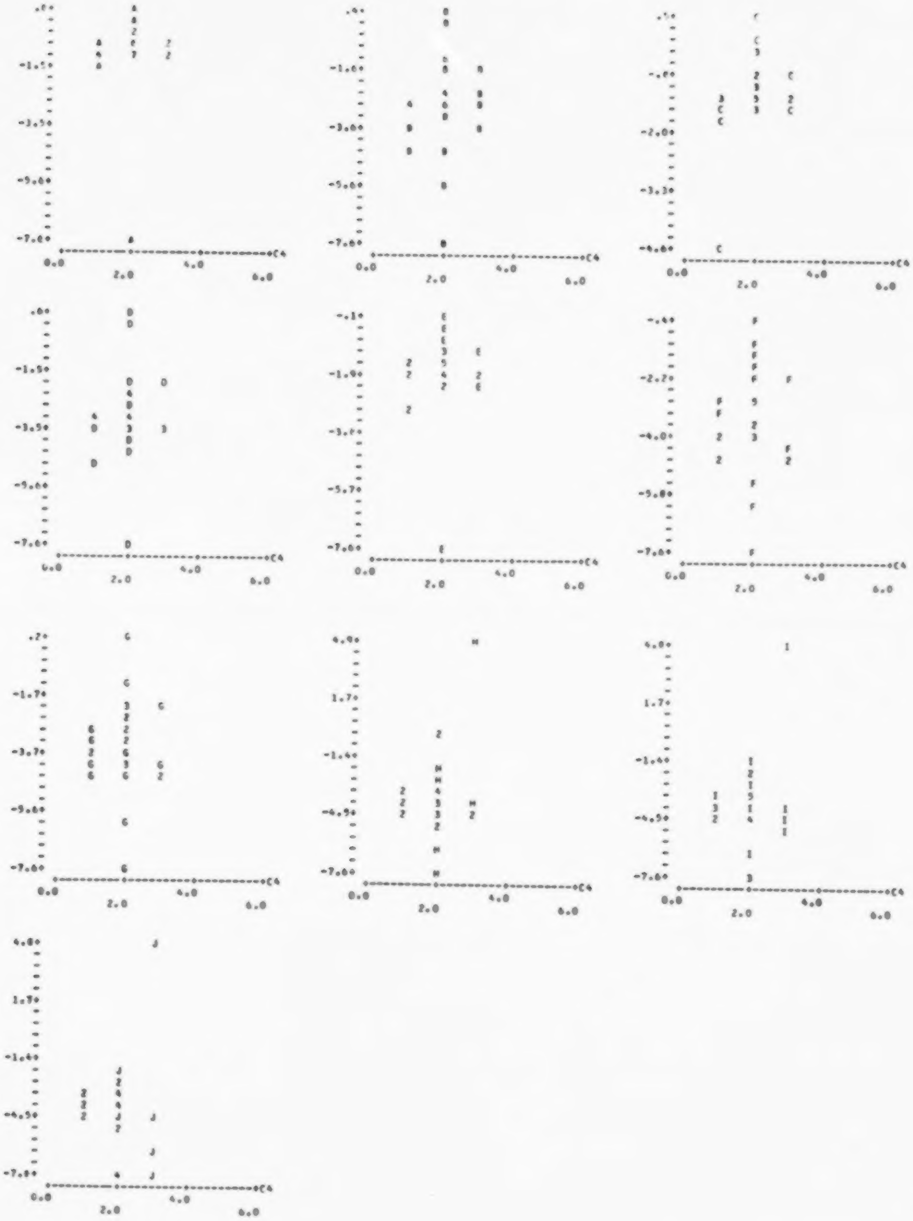

Figure C-24 Laboratory averages for $\log_e$ transformed chromium data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-26-1 METHODS USED IN THE DETERMINATION OF CADMIUM

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry - Direct Aspiration	7	103 to 257
2	A.A.S. (direct?)	17	13 to 249
3	A.A.S. Graphite Furnace	3	27 to 67.5

TABLE C-26-3. LABORATORY RANK SUMS FOR LOG_e CADMIUM DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	86.5	13	119.5	30	76.5
4	257	18	140.5	34	102.5
5	256.5	19	146	37	173
6	100	20	225	40	106
7	97.5	21	194.5	42	67
8	27	23	144.5	46	249
9	13	25	103	48	164
10	62.5	28	156.5	49	225.5
12	161	29	208.5	50	117.5

TABLE C-26-2 ORDERED LABORATORY RANK SUMS FOR $\log_e$ CADMIUM DATA

Ordered Rank Sums	Method Code Number 1	2	3
13		9	
27			8
62.5			10
67			42
---------*			
76.5		30	
86.5		2	
97.5		7	
100		6	
102.5		34	
103	25		
106		40	
117.5	50		
119.5		13	
140.5		18	
144.5		23	
146		19	
156.5		28	
161		12	
164	48		
173		37	
194.5	21		
208.5		29	
---------*			
225		20	
225.5	49		
249		46	
256.5	5		
257	4		

* Rank sums below 69 or above 211 are extreme scores.

The A.A.S.-Graphite Furnace method appears to give lower results than the A.A.S.-Direct Aspiration and A.A.S. (direct?) methods. This conclusion is tentative however as only three laboratories used the A.A.S.-Graphite Furnace method. The A.A.S.-Direct Aspiration method appears to give slightly higher results than the A.A.S. (direct?) method.

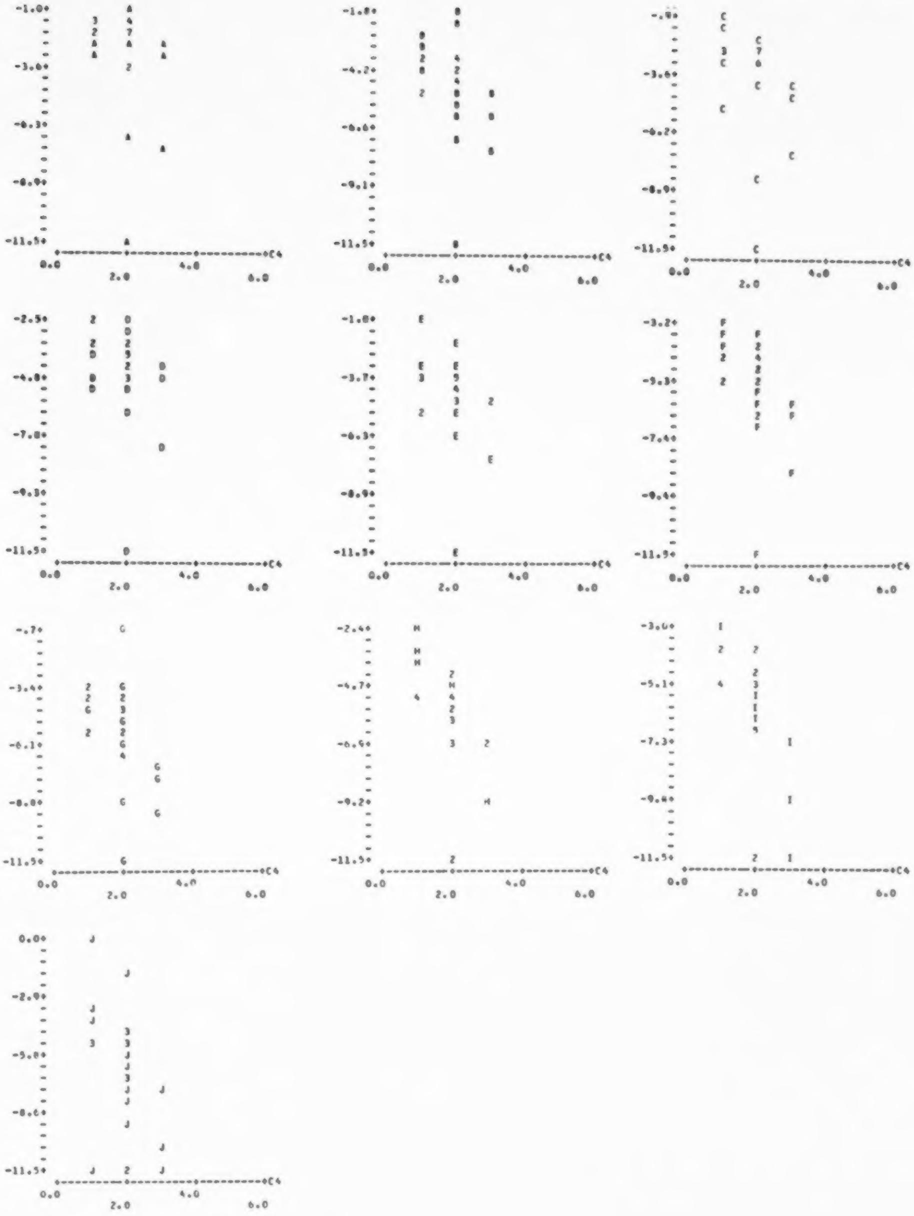

Figure C-25. Laboratory averages for $\log_e$ transformed cadmium data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-27-1 METHODS USED IN THE DETERMINATION OF COPPER

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry - Direct Aspiration	6	59.5 to 212
2	A.A.S. - (direct?)	19	14 to 254
3	A.A.S. - Graphite Furnace	4	66.5 to 216

TABLE C-27-3 . LABORATORY RANK SUMS FOR LOG$_e$ COPPER DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
1	216	13	174.5	30	154
2	251	15	168	34	181.5
4	166	18	93	37	182
5	212	19	102	40	66.5
6	58.5	20	134	42	192
7	45	21	158.5	46	172.5
8	254.5	23	95	48	150.5
9	14	25	59.5	49	129
10	188.5	28	197	50	200
12	195	29	140		

TABLE C-27-2 ORDERED LABORATORY RANK SUMS FOR LOG_e COPPER DATA

Ordered Rank Sums	Method Code Number 1	2	3
14		9	
45		7	
58.5		6	
59.5	25		
66.5			40
---------*			
93		18	
95		23	
102		19	
129	49		
134	20		
140		29	
150.5	48		
154		30	
158.5		21	
166			4
168		15	
172.5		46	
174.5		13	
181.5		34	
182		37	
188.5		10	
192			42
195		12	
197		28	
200	50		
212	5		
216			1
---------*			
251		2	
254.5		8	

* Rank sums below 73 or above 227 are extreme scores.

The A.A.S.-Direct Aspiration, A.A.S. (direct?), and A.A.S.-Graphite Furnace methods all appear to give similar results. The variability of the A.A.S.-Graphite Furnace method is perhaps larger than the other methods.

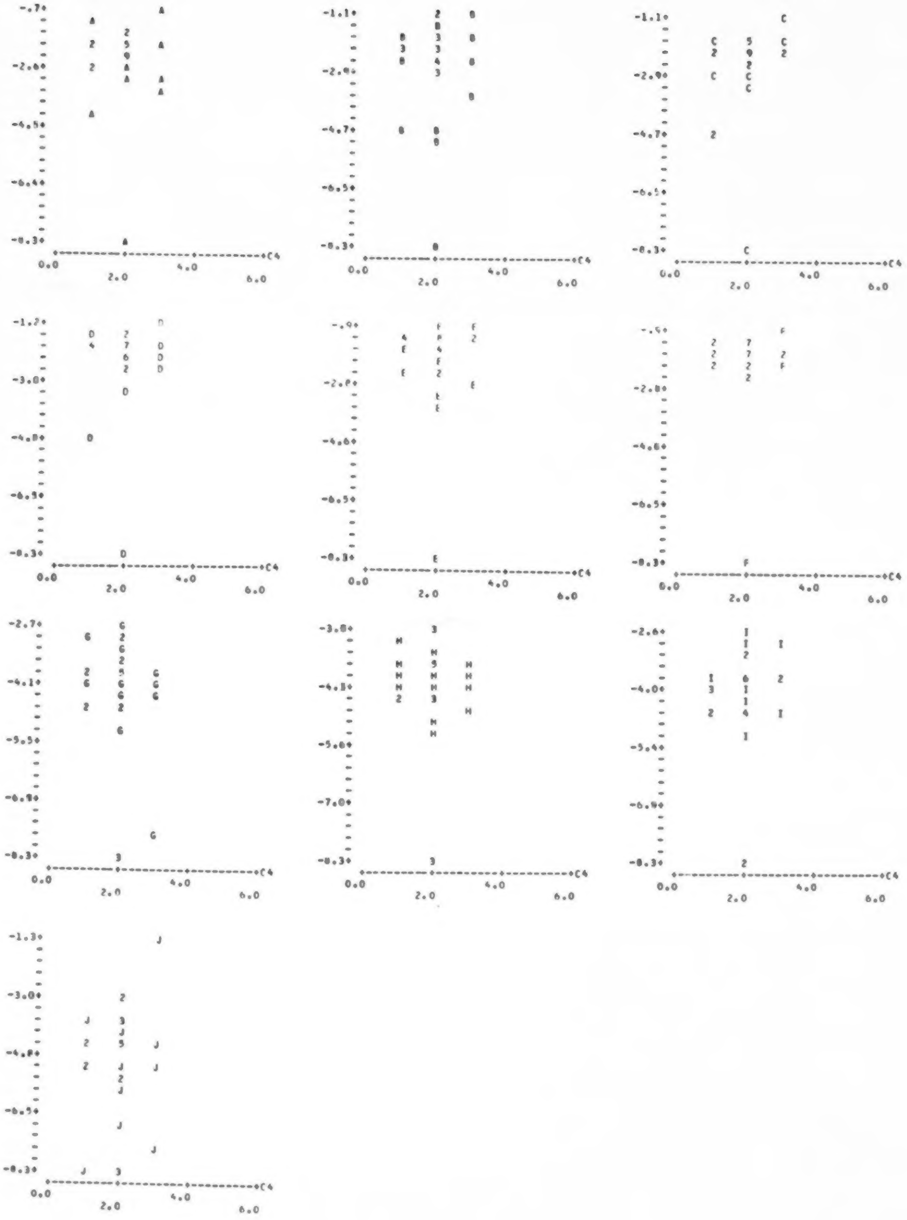

Figure C-26. Laboratory averages for $\log_e$ transformed copper data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.

TABLE C-28-1 METHODS USED IN THE DETERMINATION OF NICKEL

Method Code No.	Method	Number of labs	Rank sums scored by method
1	Atomic Absorption Spectrophotometry - Direct Aspiration	6	109 to 229
2	A.A.S. (direct?)	18	43.5 to 277
3	A.A.S. - Graphite Furnace	4	44 to 207

TABLE C-28-3. LABORATORY RANK SUMS FOR LOG_e NICKEL DATA

Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored	Laboratory Number	Rank Sum Scored
2	95	15	277	30	77.5
4	207	18	115	34	113.5
5	229	19	165	37	236
6	105.5	20	204	40	151
7	54.5	21	156.5	42	44
8	159	23	171	46	254
9	43.5	25	153.5	48	178.5
10	116.5	28	137	49	184.5
12	134.5	29	113	50	109
13	75.5				

TABLE C-28-2 ORDERED LABORATORY RANK SUMS FOR LOG$_e$ NICKEL DATA

Ordered Rank Sums	Method Code Number 1	2	3
43.5		9	
44			42
54.5		7	
----------*			
75.5		13	
77.5			30
95		2	
105.5			6
109	50		
113		29	
113.5		34	
115		18	
116.5		10	
134.5		12	
137		28	
151		40	
153.5	25		
156.5	21		
159		8	
165		19	
171		23	
178.5	48		
184.5	49		
204		20	
207			4
----------*			
229	5		
236		37	
254		46	
277		15	

* Rank sums below 71 or above 219 are extreme scores.

The A.A.S.-Graphite Furnace method appears to give slightly lower results than the other methods, however the somewhat high rank sum scored by one of the laboratories using this method makes this conclusion very tenuous. The A.A.S.-Direct Aspiration and A.A.S. (direct?) appear to give similar results.

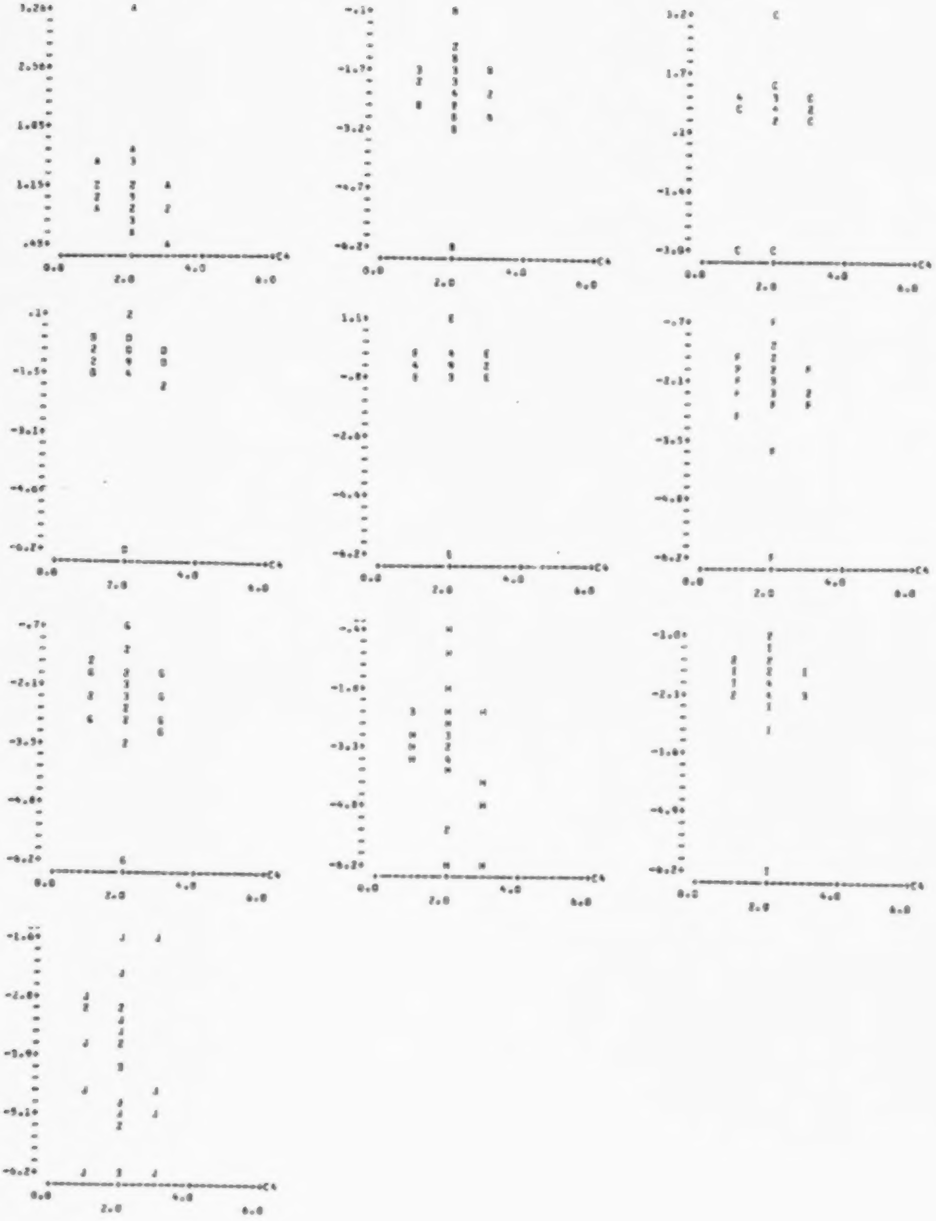

Figure C-27 Laboratory averages for $\log_e$ transformed nickel data (vertical axis) plotted against the method code number (horizontal axis) for leachate samples A through J respectively.